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(54) MODIFICATION OF SURFACE LAYER OF RESIN MOLDED MATERIAL, DEVICE THEREFOR AND RESIN MOLDED MATERIAL OF WHICH SURFACE LAYER IS MODIFIED, AND COLORING OF SURFACE LAYER OF RESIN MOLDED MATERIAL, DEVICE THEREFOR AND RESIN MOLDED MATERIAL OF WHICH SURFACE LAYER IS COLORED, AND RESIN FORMED MATERIAL IMPARTED WITH FUNCTIONALITY BY SURFACE MODIFICATION

(57)Abstract:

PROBLEM TO BE SOLVED: To perform a modification and/or coloring of a resin surface layer by penetrating/dispersing an organic compound having an affinity to the resin and a sublimating property on the surface of the resin formed material.

SOLUTION: This method for modifying and coloring a surface of a resin is provide by

putting a resin formed material and an organic compound having an affinity to the resin and also a sublimating property in a hermetically closed container, and adjusting inside pressure and temperature to make a saturated sublimation pressure state for uniformly attaching the organic compound on the surface of the resin formed material and further penetrating/dispersing to its inside. Also, by modifying the surface of the resin, it is possible to impart functionality to it.

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CLAIMS

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[Claim(s)]

[Claim 1] The reforming approach of the resin moldings surface layer characterized by to permeate and distribute said organic compound which laid the resin of the resin moldings which has sublimability and is covered, the organic compound which has compatibility, and said resin moldings in the closed space, put the inside of said closed space on the saturation sublimation-pressure condition of said organic compound, and said organic compound steam was made to adhere to homogeneity on said resin moldings front face, and adhered from said resin moldings front face to the interior.

[Claim 2] It lays in the space C which closed the organic compound which has the resin and compatibility of the resin moldings which has sublimability and is covered. On the other hand, lay in the space J which closed said resin moldings, and the temperature in the closed space J It controls identically to the temperature in the closed space C more highly than the temperature in the closed space C. The pressure in the closed space C is put on the saturation sublimation pressure condition of said organic compound, and the pressure in the closed space J is controlled identically to the pressure in the closed space C lower than the pressure in the closed space C. Subsequently Make the closed space C and the closed space J connect, and it considers as the closed space M with which the closed space C and the closed space J were aligned. Furthermore, temperature and a pressure are controlled so that the whole inside of closed space M will be in the saturation sublimation pressure condition of said organic compound. It is made to be spread in the space J closed before the steam of said organic compound which it was full of in the space C closed before connection connecting. The reforming approach of the resin moldings surface layer characterized by permeating and distributing said organic compound which said organic compound steam was made to adhere to homogeneity on said resin moldings front face, and adhered from said resin moldings front face to the interior.

[Claim 3] It is the reforming approach of the resin surface layer which is at least one mode chosen from the groups which consist of five modes of the following (A) - (E), and is characterized by adhering or containing in the source substrate of sublimation so that said organic compound can adhere to said resin moldings front face in the reforming approach of a resin moldings surface layer according to claim 1.

(A) said organic compound -- independent -- the front face of the source substrate of sublimation -- coating -- or membranes are formed -- (B) -- said organic compound and binder resin -- the front face of the source substrate of sublimation -- coating -- or membranes are formed -- (C) -- the porosity particle which has sunk in said organic compound -- the front face of the source substrate of sublimation -- coating -- or membranes are formed -- (D) That which sank into the front face of the source substrate of sublimation in the porosity particle and binder resin which have sunk in said organic compound, and sank into the hole of coating or the source substrate front face of sublimation of (E) porosity currently formed in said organic compound.

[Claim 4] The reforming approach of the resin surface layer characterized by setting to the reforming approach of a resin surface layer according to claim 3, and arranging the front face of said source substrate of sublimation which adheres or contains said organic compound on the front face in one mode of above-mentioned (A) - (E) near said resin moldings front face.

[Claim 5] In the reforming approach of a resin surface layer according to claim 1, said resin moldings and said organic compound are put into a vacuum housing. It exhausts from the vacuum

valve prepared in said vacuum housing. The pressure in said vacuum housing It decompresses to the saturation sublimation pressure of said organic compound in the temperature which is beyond a room temperature and does not exceed the pyrolysis temperature of said organic compound and/or said resin. It considers as the space which sealed and closed all the vacuum valves prepared in said vacuum housing. The reforming approach of the resin surface layer characterized by heating the temperature inside said sealed vacuum housing to the temperature to which the partial pressure of said organic compound reaches saturation sublimation pressure in the above-mentioned reduced pressure condition, and annealing said vacuum housing after predetermined time heating.

[Claim 6] Said organic compound which set to the reforming approach of a resin surface layer according to claim 3, and was adhered or contained in the source substrate of sublimation in said one of modes according to claim 3, and said resin moldings It puts into a vacuum housing and exhausts from the vacuum valve prepared in said vacuum housing. The pressure in said vacuum housing It decompresses to the saturation sublimation pressure of said organic compound in the temperature which is beyond a room temperature and does not exceed the pyrolysis temperature of said organic compound and/or said resin. It considers as the space which sealed and closed all the vacuum valves prepared in said vacuum housing. The reforming approach of the resin surface layer characterized by heating the temperature inside said sealed vacuum housing to the temperature to which the partial pressure of said organic compound reaches saturation sublimation pressure in the above-mentioned reduced pressure condition, and annealing said vacuum housing after predetermined time heating.

[Claim 7] Said organic compound which set to the reforming approach of a resin surface layer according to claim 4, and was adhered or contained in the source substrate of sublimation in said one of modes according to claim 3, and said resin moldings It puts into a vacuum housing and exhausts from the vacuum valve prepared in said vacuum housing. The pressure in said vacuum housing It decompresses to the saturation sublimation pressure of said organic compound in the temperature which is beyond a room temperature and does not exceed the pyrolysis temperature of said organic compound and/or said resin. The reforming approach of the resin surface layer characterized by considering as the space which sealed and closed all the vacuum valves prepared in said vacuum housing, heating the temperature inside said sealed vacuum housing to the temperature to which the partial pressure of said organic compound reaches saturation sublimation pressure in the above-mentioned reduced pressure condition, and annealing it after predetermined time heating.

[Claim 8] In the reforming approach of a resin surface layer according to claim 1, said resin moldings and said organic compound are put into a vacuum housing. Heating to the temperature which is beyond a room temperature about the temperature inside said vacuum housing, and does not exceed the pyrolysis temperature of said organic compound and/or said resin, and maintaining at the above-mentioned temperature It exhausts from the vacuum valve prepared in said vacuum housing. The pressure in said vacuum housing The reforming approach of the resin surface layer which decompresses to the saturation sublimation pressure of said organic compound in the above-mentioned temperature, considers as the space which sealed and closed all the vacuum valves prepared in said vacuum housing, and is characterized by annealing said vacuum housing after predetermined time heating reduced pressure.

[Claim 9] Said organic compound which set to the reforming approach of a resin surface layer according to claim 3, and was adhered or contained in the source substrate of sublimation in said one of modes according to claim 3, and said resin moldings Putting into a vacuum housing, heating to the temperature which is beyond a room temperature about the temperature inside said vacuum housing, and does not exceed the pyrolysis temperature of said organic compound and/or said resin, and maintaining at the above-mentioned temperature It exhausts from the vacuum valve prepared in said vacuum housing. The pressure in said vacuum housing The reforming approach of the resin surface layer which decompresses to the saturation sublimation pressure of said organic compound in the above-mentioned temperature, considers as the space which sealed and closed all the vacuum valves prepared in said vacuum housing, and is characterized by annealing said vacuum housing after predetermined time heating reduced pressure.

[Claim 10] Said organic compound which set to the reforming approach of a resin surface layer according to claim 4, and was adhered or contained in the source substrate of sublimation in said one of modes according to claim 3, and said resin moldings Putting into a vacuum housing, heating to the temperature which is beyond a room temperature about the temperature inside said vacuum housing,

and does not exceed the pyrolysis temperature of said organic compound and/or said resin, and maintaining at the above-mentioned temperature It exhausts from the vacuum valve prepared in said vacuum housing. The pressure in said vacuum housing The reforming approach of the resin surface layer which decompresses to the saturation sublimation pressure of said organic compound in the above-mentioned temperature, considers as the space which sealed and closed all the vacuum valves prepared in said vacuum housing, and is characterized by annealing said vacuum housing after predetermined time heating reduced pressure.

[Claim 11] The organic compound which has the resin and compatibility of the resin moldings which has sublimability and is covered in the reforming approach of a resin surface layer according to claim 2 It puts into the vacuum housing C1 which prepared the connecting piping to piping, said organic compound induction, and the vacuum housing J1 to an exhaust air system. After closing the connecting piping to said organic compound induction and vacuum housing J1, from said exhaust air system the pressure in a vacuum housing C1 It decompresses to the saturation sublimation pressure of said organic compound in the temperature which is beyond a room temperature and does not exceed the pyrolysis temperature of said organic compound and/or said resin. The temperature in a vacuum housing C1 is heated to said temperature. On the other hand, said resin moldings It puts in in the vacuum housing J1 which prepared the connecting piping to piping, said resin moldings induction, and the vacuum housing C1 to an exhaust air system. The connecting piping to said resin moldings induction and vacuum housing C1 is closed. The temperature in a vacuum housing J1 It controls identically to the temperature in a vacuum housing C1 more highly than the temperature in a vacuum housing C1. The pressure in a vacuum housing C1 is put on the saturation sublimation pressure condition of said organic compound, and the pressure in a vacuum housing J1 is controlled identically to the pressure in a vacuum housing C1 lower than the pressure in a vacuum housing C1. Subsequently A vacuum housing C1 and a vacuum housing J1 are made to connect through mutual connecting piping. It considers as the closed space M with which the space C closed in the vacuum housing C1 and the space J closed in the vacuum housing J1 were aligned. Furthermore, temperature and a pressure are controlled so that the whole inside of closed space M will be in the saturation sublimation pressure condition of said organic compound. It is made to be spread in the vacuum housing J1 before the steam of said organic compound which it was full of in the vacuum housing C1 before connection connecting. In order to make the interior permeate and distribute said organic compound which said organic compound steam was made to adhere to homogeneity on said resin moldings front face, and adhered from said resin moldings front face, after carrying out predetermined time heating, The connecting piping which has connected the vacuum housing C1 and the vacuum housing J1 mutually is closed. Predetermined time control of the temperature and the pressure in a vacuum housing J1 is carried out so that the steam of said organic compound which remains to the vacuum housing J1 interior may permeate and distribute inside from said resin moldings front face. It is the reforming approach of the resin surface layer which discharges from an exhaust air system to the vacuum housing J1 exterior when the steam of said organic compound exists in the vacuum housing J1 interior superfluously, and is characterized by subsequently returning the temperature of said resin moldings in a vacuum housing J1 to ordinary temperature.

[Claim 12] The reforming approach of the resin surface layer which adjoins a vacuum housing J1 through a gate valve, is prepared and is characterized independently by returning the temperature of said resin moldings to ordinary temperature after transporting said resin moldings under reduced pressure into the controllable pressure vacuum housing J2 in the reforming approach of a resin surface layer according to claim 11 instead of returning the temperature of said resin moldings in a vacuum housing J1 to ordinary temperature in a culmination.

[Claim 13] Claim 5, claim 6, claim 7, claim 8, claim 9, claim 10, claim 11, Or in order to make the interior permeate and distribute said organic compound which said organic compound steam was made to adhere to homogeneity on said resin moldings front face, and adhered in the reforming approach of a resin surface layer according to claim 12 from said resin moldings front face The reforming approach of the resin surface layer characterized by heating to the temperature which is more than the glass transition temperature of said resin about the temperature of said resin moldings, and does not exceed the pyrolysis temperature of said organic compound and/or said resin.

[Claim 14] Claim 1, claim 2, claim 3, claim 4, claim 5, claim 6, claim 7, claim 8, claim 9, claim 10, claim 11, In the reforming approach of a resin surface layer according to claim 12 or as said organic

compound The coloring approach of the resin surface layer characterized by coloring at the same time it reforms the surface layer of said resin moldings by using the coloring matter which has the resin and compatibility of the resin moldings which has sublimability and is covered.

[Claim 15] The coloring approach of the resin surface layer characterized by coloring at the same time it reforms the surface layer of said resin moldings by using the coloring matter which has the resin and compatibility of the resin moldings which has sublimability and is covered as said organic compound in the reforming approach of a resin surface layer according to claim 13.

[Claim 16] The container in which sealing for putting the organic compound which has the resin and compatibility of the resin moldings which has sublimability and is covered, and said resin moldings on the saturation sublimation pressure condition of said organic compound is possible, The reformer of the resin surface layer characterized by establishing the exhaust air system for adjusting the pressure of the container in which said sealing is possible, and a heating means for said organic compound permeating and distributing in said resin moldings further after said organic compound sublimates and the steam of an organic compound adheres to said resin moldings front face.

[Claim 17] The reformer of the resin surface layer which is the reformer of a resin moldings surface layer according to claim 16, and is further characterized by forming the source substrate of sublimation for being held in at least one mode chosen from the groups which consist of the five above-mentioned modes so that said organic compound can adhere to said resin moldings front face.

[Claim 18] The vacuum housing C1 in which sealing for putting the organic compound which has the resin and compatibility of the resin moldings which has sublimability and is covered on a saturation sublimation pressure condition is possible, The vacuum housing J1 in which sealing for putting said resin moldings on the saturation sublimation pressure condition of said organic compound is possible, The connecting piping which makes a vacuum housing C1 and a vacuum housing J1 connect mutually, and the breaker style of said connecting piping, The exhaust air system which adjusts independently the pressure in a vacuum housing C1, and the exhaust air system which adjusts independently the pressure in a vacuum housing J1, The reformer of the resin surface layer characterized by establishing a heating means for said organic compound permeating and distributing in said resin moldings further after said organic compound sublimated and the steam of an organic compound adhered to said resin moldings front face.

[Claim 19] The reformer of the resin surface layer which is the reformer of claim 16, claim 17, or a resin surface layer according to claim 18, and is characterized by establishing the device for agitating said powder-like resin moldings.

[Claim 20] The reformer of the resin surface layer which is the reformer of claim 16, claim 17, or a resin surface layer according to claim 18, and is characterized by establishing the device for rolling round said resin moldings of the gestalt chosen from the shape of fibrous, the shape of a fiber, and a film from a supply side reel to a recipient reel under a reduced pressure condition.

[Claim 21] The container in which sealing for putting the coloring matter which has the resin and compatibility of the resin moldings which has sublimability and is colored, and said resin moldings on the saturation sublimation pressure condition of said coloring matter is possible, Coloring equipment of the resin surface layer characterized by establishing the exhaust air system for adjusting the pressure of the container in which said sealing is possible, and a heating means for said coloring matter permeating and distributing in said resin moldings further after said coloring matter sublimates and the steam of coloring matter adheres to said resin moldings front face.

[Claim 22] Coloring equipment of the resin surface layer which is coloring equipment of a resin moldings surface layer according to claim 21, and is further characterized by forming the source substrate of sublimation for being held in at least one mode chosen from the groups which consist of the five above-mentioned modes so that said coloring matter can adhere to said resin moldings front face.

[Claim 23] The vacuum housing C1 in which sealing for putting the coloring matter which has the resin and compatibility of the resin moldings which has sublimability and is colored on a saturation sublimation pressure condition is possible, The vacuum housing J1 in which sealing for putting said resin moldings on the saturation sublimation pressure condition of said coloring matter is possible, The connecting piping which makes a vacuum housing C1 and a vacuum housing J1 connect mutually, and the breaker style of said connecting piping, The exhaust air system which adjusts independently the pressure in a vacuum housing C1, and the exhaust air system which adjusts

independently the pressure in a vacuum housing J1, Coloring equipment of the resin surface layer characterized by establishing a heating means for said coloring matter permeating and distributing in said resin moldings further after said coloring matter sublimated and the steam of coloring matter adhered to said resin moldings front face.

[Claim 24] Coloring equipment of the resin surface layer which is claim 21, claim 22, or coloring equipment of a resin surface layer according to claim 23, and is characterized by establishing the device for agitating said powder-like resin moldings.

[Claim 25] Coloring equipment of the resin surface layer which is claim 21, claim 22, or coloring equipment of a resin surface layer according to claim 23, and is characterized by establishing the device for rolling round said resin moldings of the gestalt chosen from the shape of fibrous, the shape of a fiber, and a film from a supply side reel to a recipient reel under a reduced pressure condition.

[Claim 26] The resin formation object characterized by carrying out reforming of the surface layer by the reforming approach of claim 1, claim 2, claim 3, claim 4, claim 5, claim 6, claim 7, claim 8, claim 9, claim 10, claim 11, or a resin surface layer according to claim 12.

[Claim 27] The resin formation object characterized by carrying out reforming of the surface layer by the reforming approach of a resin surface layer according to claim 13.

[Claim 28] The resin formation object characterized by coloring a surface layer by the coloring approach of a resin surface layer according to claim 14.

[Claim 29] The resin formation object characterized by coloring a surface layer by the coloring approach of a resin surface layer according to claim 15.

[Claim 30] The plastic lens characterized by carrying out reforming of the surface layer by the reforming approach of claim 1, claim 2, claim 3, claim 4, claim 5, claim 6, claim 7, claim 8, claim 9, claim 10, claim 11, or a resin surface layer according to claim 12.

[Claim 31] The plastic lens characterized by coloring a surface layer by the coloring approach of a resin surface layer according to claim 14.

[Claim 32] The resin coat lens characterized by carrying out reforming of the resin surface layer by the reforming approach of claim 1, claim 2, claim 3, claim 4, claim 5, claim 6, claim 7, claim 8, claim 9, claim 10, claim 11, or a resin surface layer according to claim 12.

[Claim 33] The resin coat lens characterized by coloring a resin surface layer by the coloring approach of a resin surface layer according to claim 14.

[Claim 34] Plastic film characterized by carrying out reforming of the surface layer by the reforming approach of claim 1, claim 2, claim 3, claim 4, claim 5, claim 6, claim 7, claim 8, claim 9, claim 10, claim 11, or a resin surface layer according to claim 12.

[Claim 35] Plastic film characterized by coloring a surface layer by the coloring approach of a resin surface layer according to claim 14.

[Claim 36] Fiber characterized by carrying out reforming of the surface layer by the reforming approach of claim 1, claim 2, claim 3, claim 4, claim 5, claim 6, claim 7, claim 8, claim 9, claim 10, claim 11, or a resin surface layer according to claim 12.

[Claim 37] Fiber characterized by coloring a surface layer by the coloring approach of a resin surface layer according to claim 14.

[Claim 38] The plastic optical fiber characterized by carrying out reforming of the surface layer by the reforming approach of claim 1, claim 2, claim 3, claim 4, claim 5, claim 6, claim 7, claim 8, claim 9, claim 10, claim 11, or a resin surface layer according to claim 12.

[Claim 39] The plastic optical fiber characterized by coloring a surface layer by the coloring approach of a resin surface layer according to claim 14.

[Claim 40] The resin formation object characterized by giving a firefly luminescence function to a surface layer by surface layer reforming using the fluorochrome which has the resin and compatibility of claim 1, claim 2, claim 3, claim 4, claim 5, claim 6, claim 7, claim 8, claim 9, claim 10, claim 11 or the reforming approach of a resin surface layer according to claim 12, and the resin moldings that has sublimability and is covered.

[Claim 41] The resin formation object characterized by giving a photochromic function to a surface layer by surface layer reforming using the photochromic coloring matter which has the resin and compatibility of claim 1, claim 2, claim 3, claim 4, claim 5, claim 6, claim 7, claim 8, claim 9, claim 10, claim 11 or the reforming approach of a resin surface layer according to claim 12, and the resin

[Claim 45] Claim 1, claim 2, claim 3, claim 4, claim 5, claim 6, claim 7, claim 8, claim 9, claim 10, claim 11, By or surface layer reforming using the organic compound in which it has the reforming approach of a resin surface layer according to claim 12, and the resin and compatibility of a resin moldings which have sublimability and are covered, and bioactive is shown to animals and plants The resin formation object characterized by giving the function as agricultural chemicals to a surface layer.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the resin moldings with which the equipment and the surface layer the coloring approach of the resin moldings with which reforming of the equipment and the surface layer the reforming approach of a resin moldings surface layer and for it was carried out, and a resin moldings surface layer, and for it were colored, and the resin moldings to which functionality was given by reforming of a surface layer.

[0002]

[Description of the Prior Art] As the reforming approach of the [reforming approach of resin surface layer] resin moldings, the approach of irradiating electromagnetic waves, such as an X-ray and a gamma ray, is learned, for example. However, the reforming approach which reforms the "surface layer" ranging from the front face to a certain depth of a resin moldings, and is not reformed about the interior of a resin moldings is not only restricted very much, but is accompanied by many constraint.

[0003] For example, although the approach of driving the ion beam of a metal or an organic compound into a resin front face is learned, there is constraint of the organic compound with it difficult [ for processing the whole resin film of a large area to homogeneity to process the whole front face of the difficult resin moldings of a complicated configuration to homogeneity ] which can be used as an ion beam being restricted.

[0004] For example, although the approach (the laser ablation method) of carrying out the short-time exposure of the laser pulse of a high-power consistency on a resin front face, and reforming a front face is learned, there is constraint with it difficult [ for processing the whole resin film of a large area to homogeneity to process the whole front face of the difficult resin moldings of a complicated configuration to homogeneity ].

[0005] For example, although the approach of carrying out plasma treatment of the resin front face under atmospheric pressure, and oxidizing and reforming a front face is learned, constraint of that it is inapplicable, effectiveness not lasting long is shown in the front face which cannot oxidize easily.

[0006] When the processing agent for reforming a resin surface layer is a liquid, coating can be carried out to the front face of a resin moldings, on the other hand, when it is a solid-state, coating can be carried out as a solution using a suitable solvent, and the approach of soaking a resin moldings into a solution can be taken. However, the such wet approach has constraint of there being a possibility that a resin front face may swell with a solvent, when using a solvent with a possibility that the effectiveness of surface treatment may be spoiled in case it is washing to be washed in order to make it a superfluous processing agent not remain in the resin front face on which the smooth nature and the fine structure on the front face of resin are easy to be lost.

[0007] Moreover, although the approach of mixing and kneading the processing agent for reforming a resin surface layer, and fabricating it to the whole resin is also used widely Properly speaking, it is necessary to mix a processing agent required only for a surface layer to the whole resin. in order to make it the processing agent mixed to the whole resin with which the processing agent mixed to the whole resin may have a bad influence on the physical properties of resin not have a bad influence on the physical properties of resin -- the need -- enough -- there are problems, like the class of processing agent mixed to the whole resin which cannot add an amount has constraint.

[0008] [-- resin -- a moldings -- a front face -- coloring -- an approach --] -- resin -- a moldings -- coloring -- an approach -- \*\*\*\*\* -- for example -- resin -- inside -- a color -- or -- a pigment -- having kneaded -- after -- (-- one --) -- injection molding -- carrying out -- coloring -- having had -- resin -- a moldings -- obtaining -- an approach -- (-- two --) -- extension -- carrying out -- coloring -- having had -- a film -- \*\* -- a thing -- obtaining -- an approach -- (-- three --) -- spinning -- carrying out -- being fibrous -- a thing -- obtaining -- an approach -- etc. etc. -- large -- using -- having -- \*\*\*\*.

[0009] On the other hand, as an approach of coloring only a front face, various kinds of coating methods and print processes are used widely, without changing the presentation inside a resin moldings.

[0010] Only the coloring matter of the property which permeates a resin surface layer is made to adhere to a resin moldings front face in a coating method or print processes, and, in the case of the usual coating method or print processes, the layer which consists of mixture of binder resin, a color, or a pigment is formed in a resin front face except for the case of a special approach which is made to permeate. When it says strictly, such a coloring approach is not "coloring of the front face itself" but "making the colored film add and adhere to a front face." Therefore, when micro processing is made on the resin front face, there is a problem referred to as that micro processing will be buried with the added film. Moreover, when using a coating method, there is a possibility that the smooth nature of a resin moldings front face etc. may be spoiled by the dissolution and swelling by the coating solvent. Then, if it is going to avoid the dissolution and swelling of a resin surface layer, a suitable coating solvent may not be found but application of a coating method may become difficult. For example, the solvent which will dissolve Pori (methyl methacrylate) in it if it is going to produce the film which consists of coloring matter and Pori (methyl methacrylate) by the coating method using a solvent on the front face of the resin moldings which consists of Pori (methyl methacrylate) is not easy to surely corrode the front face of the resin moldings which consists of Pori (methyl methacrylate), and to acquire a smooth coating side.

[0011] When the coating film or printing film containing the coloring matter of sublimability is made to adhere to a resin front face and it is going to color it it, there are the still more nearly following problems.

[0012] (i) Coating thru/or when printing, sublimability coloring matter may sublimate the constituent which consists of sublimability coloring matter and resin in the middle of a process. For this reason, the control for equalizing the control and the presentation for carrying out a presentation to regularity is not easy.

[0013] (ii) It is very difficult to make only sublimability coloring matter remain and to remove other volatile impurities. Therefore, it is not easy to produce the coating film and printing film which does not contain volatile impurities other than sublimability coloring matter.

[0014] The vacuum evaporatio film of sublimability coloring matter other than the approach of forming the coating film and the printing film in a resin front face can be formed, and a resin moldings can also be colored. Temperature of the source of vacuum evaporatio is made higher than the temperature of the substrate formed membranes, and the organic compound steam which came flying from the source of vacuum evaporatio is made to deposit on a low-temperature formed membranes substrate front face more in the usual vacuum deposition. In the membrane formation approach under such a non-equilibrium condition, thickness control is chiefly performed by the mechanical means. That is, a mask or a slit is installed in the space from the source of vacuum evaporatio to the substrate formed membranes, and the concentration of an organic compound steam is controlled spatially, and it performs rotating the substrate formed membranes etc., and equalization of the thickness of the vacuum evaporatio film is attained. However, when the vapor pressure of an organic compound (coloring matter) is high and it is easy to sublimate it, it is not easy to make thickness of the vacuum evaporatio film into homogeneity only by such mechanical means.

[0015] The sublimation replica method is known as the image printing approach using sublimation. That is, it is the approach of making it deposit and permeate to the imprint layer on the front face of paper which was made to heat and sublimate the sublimability coloring matter formed by the front face of a sublimation imprint ribbon or a sheet with a heating head, and was established in near (thin

film which consists of thermoplastics). It is theoretically equivalent to vacuum deposition, and the shade of an image is controlled by the heating area and the amount of heating in a heating head. Therefore, although it is suitable for the application which prints the image which has detailed gradation by the principle of "sketch drawing", for coloring a resin front face by concentration uniform about a large area, it is unsuitable. Moreover, it is not fit for coloring of the resin moldings of the shape of complicated surface type.

[0016]

[Problem(s) to be Solved by the Invention] This invention solves the above technical problems and consists of a (a) sublimability organic compound and resin. The method of producing the surface layer by which reforming was carried out on the front face of a resin moldings with these uniform presentations, (b) Contain a sublimability organic compound and an volatile impurity is not included. It consists of the approach and (c) sublimability organic compound which produce the surface layer by which reforming was carried out on the front face of a resin moldings, and resin. The method of producing efficiently the surface layer by which reforming was carried out on the front face of a resin moldings with these uniform presentations, (d) Contained the sublimability organic compound, without spoiling the surface smooth nature of a resin moldings. When micro processing is performed to the front face of the approach of producing the surface layer by which reforming was carried out on the front face of a resin moldings, and (e) resin moldings, The approach of producing the surface layer by which reforming was carried out on the front face of a resin moldings which contained the sublimability organic compound, without spoiling this surface structure, (f) The approach containing the sublimability organic compound of an extensive class of producing the surface layer by which reforming was carried out on the front face of a resin moldings, (g) Contained thickness and/or a sublimability organic compound with a uniform presentation without complicated mechanical control. It is not concerned with the size of the area of the approach of producing the surface layer by which reforming was carried out on the front face of a resin moldings, and the (h) surface layer. Contained the sublimability organic compound which has uniform thickness and/or a uniform presentation. The equipment for producing the approach of producing the surface layer by which reforming was carried out on the front face of a resin moldings, and the surface layer which has the description of (i) above-mentioned (a) - (h) and by which reforming was carried out on the front face of a resin moldings, (j) A resin moldings with the surface layer which has the description of above-mentioned (a) - (h) and by which reforming was carried out, (k) How to consist of sublimability coloring matter and resin and to produce the colored surface layer with these uniform presentations on the front face of a resin moldings, (l) The approach of containing sublimability coloring matter and not containing an volatile impurity which produces the colored surface layer on the front face of a resin moldings, (m) How to consist of sublimability coloring matter and resin and to produce efficiently the colored surface layer with these uniform presentations on the front face of a resin moldings, (n) Contained sublimability coloring matter, without spoiling the surface smooth nature of a resin moldings. When micro processing is performed to the front face of the approach of producing the colored surface layer on the front face of a resin moldings, and (o) resin moldings, The approach of producing the colored surface layer on the front face of a resin moldings which contained sublimability coloring matter, without spoiling this surface structure, (p) The approach containing the sublimability coloring matter of an extensive class of producing the colored surface layer on the front face of a resin moldings, (q) Contained thickness and/or sublimability coloring matter with a uniform presentation without complicated mechanical control. It is not concerned with the size of the area of the approach of producing the colored surface layer on the front face of a resin moldings, and the (r) surface layer. The approach containing the sublimability coloring matter which has uniform thickness and/or a uniform presentation of producing the colored surface layer on the front face of a resin moldings, (s) Equipment for producing the colored surface layer which has the description of above-mentioned (k) - (r) on the front face of a resin moldings, (t) A surface layer aims at offering the resin moldings to which functionality was given by having carried out reforming of the (above-mentioned k) a resin moldings and the (u) surface layer with the colored surface layer which has the description of - (r).

[0017]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, the reforming

approach of the resin moldings surface layer concerning invention of this application according to claim 1 The resin of the resin moldings which has sublimability and is covered, and the organic compound which has compatibility, It is characterized by permeating and distributing said organic compound which laid said resin moldings in the closed space, put the inside of said closed space on the saturation sublimation pressure condition of said organic compound, and said organic compound steam was made to adhere to homogeneity on said resin moldings front face, and adhered from said resin moldings front face to the interior.

[0018] Here, saturation sublimation pressure is the vapor pressure in the fixed temperature which is also called maximum vapor tension and has a thermodynamic system, is the front face of the solid phase of the matter, and means that the vapor pressure of the matter is in equilibrium. It is not dependent on the amount of the matter and maximum vapor tension increases in monotone with the rise of temperature only depending on temperature. The situation of the change is shown by the formula of the KURAUJISU-KURAPE irone (Clausis-Clapeyron) shown below.

[0019]

[Equation 1]

$$Dp/dT=Q/T\Delta V \text{ -- (1)}$$

Here, p expresses maximum vapor tension and T expresses temperature for the difference of the volume [ in / for the heating value (heat of sublimation; the temperature of the matter does not rise by this heating-value absorption) which absorbs Q when the matter (solid-state) of unit mass becomes a gas (steam) / in  $\Delta V$  / the phase change from a solid-state to a gas ] per unit mass.

[0020] The reforming approach of the resin moldings surface layer which starts invention of this application according to claim 2 in order to attain the above-mentioned purpose It lays in the space C which closed the organic compound which has the resin and compatibility of the resin moldings which has sublimability and is covered. On the other hand, lay in the space J which closed said resin moldings, and the temperature in the closed space J It controls identically to the temperature in the closed space C more highly than the temperature in the closed space C. The pressure in the closed space C is put on the saturation sublimation pressure condition of said organic compound, and the pressure in the closed space J is controlled identically to the pressure in the closed space C lower than the pressure in the closed space C. Subsequently Make the closed space C and the closed space J connect, and it considers as the closed space M with which the closed space C and the closed space J were aligned. Furthermore, temperature and a pressure are controlled so that the whole inside of closed space M will be in the saturation sublimation pressure condition of said organic compound. It is characterized by permeating and distributing said organic compound which make it spread in the space J closed before the steam of said organic compound which it was full of in the space C closed before connection connecting, and said organic compound steam was made to adhere to homogeneity on said resin moldings front face, and adhered from said resin moldings front face to the interior.

[0021] The reforming approach of the resin moldings surface layer which starts invention of this application according to claim 3 in order to attain the above-mentioned purpose In the reforming approach of a resin moldings surface layer according to claim 1 said organic compound It is characterized by adhering or containing in the source substrate of sublimation in at least one mode chosen from the groups which consist of five modes of the following (A) - (E) so that it can adhere to said resin moldings front face.

[0022] (A) said organic compound -- independent -- the front face of the source substrate of sublimation -- coating -- or membranes are formed -- (B) -- said organic compound and binder resin -- the front face of the source substrate of sublimation -- coating -- or membranes are formed -- (C) -- the porosity particle which has sunk in said organic compound -- the front face of the source substrate of sublimation -- coating -- or membranes are formed -- (D) That which sank into the front face of the source substrate of sublimation in the porosity particle and binder resin which have sunk in said organic compound, and sank into the hole of coating or the source substrate front face of sublimation of (E) porosity currently formed in said organic compound.

[0023] The reforming approach of the resin moldings surface layer which starts invention of this application according to claim 4 in order to attain the above-mentioned purpose is characterized by setting to the reforming approach of a resin surface layer according to claim 3, and arranging the

front face of said source substrate of sublimation which adheres or contains said organic compound on the front face in one mode of above-mentioned (A) - (E) near said resin moldings front face. [0024] Here, "near" means making it approach as much as possible, unless the front face and said resin moldings front face of said source substrate of sublimation contact. For example, it is optimum that said source substrate of sublimation and said resin moldings front face make the distance between flat surfaces approach to micrometer order if surface irregularity was a less than 1-micrometer smooth flat surface. However, when the ease of the actuation at the time of surface layer reforming and coloring processing is taken into consideration, it is desirable to make it approach to several mm thru/or about 10 millimeters by making this into a minimum.

[0025] The reforming approach of the resin moldings surface layer which starts invention of this application according to claim 5 in order to attain the above-mentioned purpose In the reforming approach of a resin surface layer according to claim 1, said resin moldings and said organic compound are put into a vacuum housing. It exhausts from the vacuum valve prepared in said vacuum housing. The pressure in said vacuum housing It decompresses to the saturation sublimation pressure of said organic compound in the temperature which is beyond a room temperature and does not exceed the pyrolysis temperature of said organic compound and/or said resin. It considers as the space which sealed and closed all the vacuum valves prepared in said vacuum housing, the temperature inside said sealed vacuum housing is heated to the temperature to which the partial pressure of said organic compound reaches saturation sublimation pressure in the above-mentioned reduced pressure condition, and it is characterized by annealing said vacuum housing after predetermined time heating.

[0026] The reforming approach of the resin moldings surface layer which starts invention of this application according to claim 6 in order to attain the above-mentioned purpose Said organic compound which set to the reforming approach of a resin surface layer according to claim 3, and was adhered or contained in the source substrate of sublimation in said one of modes according to claim 3, and said resin moldings It puts into a vacuum housing and exhausts from the vacuum valve prepared in said vacuum housing. The pressure in said vacuum housing It decompresses to the saturation sublimation pressure of said organic compound in the temperature which is beyond a room temperature and does not exceed the pyrolysis temperature of said organic compound and/or said resin. It considers as the space which sealed and closed all the vacuum valves prepared in said vacuum housing, the temperature inside said sealed vacuum housing is heated to the temperature to which the partial pressure of said organic compound reaches saturation sublimation pressure in the above-mentioned reduced pressure condition, and it is characterized by annealing said vacuum housing after predetermined time heating.

[0027] The reforming approach of the resin moldings surface layer which starts invention of this application according to claim 7 in order to attain the above-mentioned purpose Said organic compound which set to the reforming approach of a resin surface layer according to claim 4, and was adhered or contained in the source substrate of sublimation in said one of modes according to claim 3, and said resin moldings It puts into a vacuum housing and exhausts from the vacuum valve prepared in said vacuum housing. The pressure in said vacuum housing It decompresses to the saturation sublimation pressure of said organic compound in the temperature which is beyond a room temperature and does not exceed the pyrolysis temperature of said organic compound and/or said resin. It is characterized by considering as the space which sealed and closed all the vacuum valves prepared in said vacuum housing, heating the temperature inside said sealed vacuum housing to the temperature to which the partial pressure of said organic compound reaches saturation sublimation pressure in the above-mentioned reduced pressure condition, and annealing it after predetermined time heating.

[0028] The reforming approach of the resin moldings surface layer which starts invention of this application according to claim 8 in order to attain the above-mentioned purpose In the reforming approach of a resin surface layer according to claim 1, said resin moldings and said organic compound are put into a vacuum housing. Heating to the temperature which is beyond a room temperature about the temperature inside said vacuum housing, and does not exceed the pyrolysis temperature of said organic compound and/or said resin, and maintaining at the above-mentioned temperature It exhausts from the vacuum valve prepared in said vacuum housing. The pressure in

said vacuum housing It decompresses to the saturation sublimation pressure of said organic compound in the above-mentioned temperature, considers as the space which sealed and closed all the vacuum valves prepared in said vacuum housing, and is characterized by annealing said vacuum housing after predetermined time heating reduced pressure.

[0029] The reforming approach of the resin moldings surface layer which starts invention of this application according to claim 9 in order to attain the above-mentioned purpose Said organic compound which set to the reforming approach of a resin surface layer according to claim 3, and was adhered or contained in the source substrate of sublimation in said one of modes according to claim 3, and said resin moldings Putting into a vacuum housing, heating to the temperature which is beyond a room temperature about the temperature inside said vacuum housing, and does not exceed the pyrolysis temperature of said organic compound and/or said resin, and maintaining at the above-mentioned temperature It exhausts from the vacuum valve prepared in said vacuum housing. The pressure in said vacuum housing It decompresses to the saturation sublimation pressure of said organic compound in the above-mentioned temperature, considers as the space which sealed and closed all the vacuum valves prepared in said vacuum housing, and is characterized by annealing said vacuum housing after predetermined time heating reduced pressure.

[0030] The reforming approach of the resin moldings surface layer which starts invention of this application according to claim 10 in order to attain the above-mentioned purpose Said organic compound which set to the reforming approach of a resin surface layer according to claim 4, and was adhered or contained in the source substrate of sublimation in said one of modes according to claim 3, and said resin moldings Putting into a vacuum housing, heating to the temperature which is beyond a room temperature about the temperature inside said vacuum housing, and does not exceed the pyrolysis temperature of said organic compound and/or said resin, and maintaining at the above-mentioned temperature It exhausts from the vacuum valve prepared in said vacuum housing. The pressure in said vacuum housing It decompresses to the saturation sublimation pressure of said organic compound in the above-mentioned temperature, considers as the space which sealed and closed all the vacuum valves prepared in said vacuum housing, and is characterized by annealing said vacuum housing after predetermined time heating reduced pressure.

[0031] The reforming approach of the resin moldings surface layer which starts invention of this application according to claim 11 in order to attain the above-mentioned purpose The organic compound which has the resin and compatibility of the resin moldings which has sublimability and is covered in the reforming approach of a resin surface layer according to claim 2 It puts into the vacuum housing C1 which prepared the connecting piping to piping, said organic compound induction, and the vacuum housing J1 to an exhaust air system. After closing the connecting piping to said organic compound induction and vacuum housing J1, from said exhaust air system the pressure in a vacuum housing C1 It decompresses to the saturation sublimation pressure of said organic compound in the temperature which is beyond a room temperature and does not exceed the pyrolysis temperature of said organic compound and/or said resin. The temperature in a vacuum housing C1 is heated to said temperature. On the other hand, said resin moldings It puts in in the vacuum housing J1 which prepared the connecting piping to piping, said resin moldings induction, and the vacuum housing C1 to an exhaust air system. The connecting piping to account resin moldings induction and a vacuum housing C1 is closed. The temperature in a vacuum housing J1 It controls identically to the temperature in a vacuum housing C1 more highly than the temperature in a vacuum housing C1. The pressure in a vacuum housing C1 is put on the saturation sublimation pressure condition of said organic compound, and the pressure in a vacuum housing J1 is controlled identically to the pressure in a vacuum housing C1 lower than the pressure in a vacuum housing C1. Subsequently A vacuum housing C1 and a vacuum housing J1 are made to connect through mutual connecting piping. It considers as the closed space M with which the space C closed in the vacuum housing C1 and the space J closed in the vacuum housing J1 were aligned. Furthermore, temperature and a pressure are controlled so that the whole inside of closed space M will be in the saturation sublimation pressure condition of said organic compound. It is made to be spread in the vacuum housing J1 before the steam of said organic compound which it was full of in the vacuum housing C1 before connection connecting. In order to make the interior permeate and distribute said organic compound which said organic compound steam was made to adhere to homogeneity on said resin

moldings front face, and adhered from said resin moldings front face, after carrying out predetermined time heating. The connecting piping which has connected the vacuum housing C1 and the vacuum housing J1 mutually is closed. Predetermined time control of the temperature and the pressure in a vacuum housing J1 is carried out so that the steam of said organic compound which remains to the vacuum housing J1 interior may permeate and distribute inside from said resin moldings front face. When the steam of said organic compound exists in the vacuum housing J1 interior superfluously, it discharges from an exhaust air system to the vacuum housing J1 exterior, and subsequently it is characterized by returning the temperature of said resin moldings in a vacuum housing J1 to ordinary temperature.

[0032] The reforming approach of the resin moldings surface layer which starts invention of this application according to claim 12 in order to attain the above-mentioned purpose In the reforming approach of a resin surface layer according to claim 11, instead of returning the temperature of said resin moldings in a vacuum housing J1 to ordinary temperature in a culmination A vacuum housing J1 is adjoined through a gate valve, it is prepared, and after transporting said resin moldings under reduced pressure into the controllable pressure vacuum housing J2, it is characterized independently by returning the temperature of said resin moldings to ordinary temperature.

[0033] The reforming approach of the resin moldings surface layer which starts invention of this application according to claim 13 in order to attain the above-mentioned purpose Claim 5, claim 6, claim 7, claim 8, claim 9, claim 10, claim 11, Or in order to make the interior permeate and distribute said organic compound which said organic compound steam was made to adhere to homogeneity on said resin moldings front face, and adhered in the reforming approach of a resin surface layer according to claim 12 from said resin moldings front face It is more than the glass transition temperature of said resin about the temperature of said resin moldings, and is characterized by heating to the temperature which does not exceed the pyrolysis temperature of said organic compound and/or said resin.

[0034] The coloring approach of the resin moldings surface layer which starts invention of this application according to claim 14 in order to attain the above-mentioned purpose Claim 1, claim 2, claim 3, claim 4, claim 5, claim 6, claim 7, claim 8, claim 9, claim 10, claim 11, Or in the reforming approach of a resin surface layer according to claim 12, it is characterized by coloring at the same time it reforms the surface layer of said resin moldings by using the coloring matter which has the resin and compatibility of the resin moldings which has sublimability and is covered as said organic compound.

[0035] The coloring approach of the resin moldings surface layer which starts invention of this application according to claim 15 in order to attain the above-mentioned purpose is characterized by coloring at the same time it reforms the surface layer of said resin moldings by using the coloring matter which has the resin and compatibility of the resin moldings which has sublimability and is covered as said organic compound in the reforming approach of a resin surface layer according to claim 13.

[0036] The reformer of the resin moldings surface layer which starts invention of this application according to claim 16 in order to attain the above-mentioned purpose The container in which sealing for putting the organic compound which has the resin and compatibility of the resin moldings which has sublimability and is covered, and said resin moldings on the saturation sublimation pressure condition of said organic compound is possible, After said organic compound sublimates with the exhaust air system for adjusting the pressure of the container in which said sealing is possible and the steam of an organic compound adheres to said resin moldings front face, said organic compound is further characterized by establishing the heating means for permeating and distributing into said resin moldings.

[0037] The reformer of the resin moldings surface layer which starts invention of this application according to claim 17 in order to attain the above-mentioned purpose is a reformer of a resin moldings surface layer according to claim 16, further, is at least one mode chosen from the groups which consist of the five above-mentioned modes, and is characterized by forming the source substrate of sublimation for being held so that said organic compound can adhere to said resin moldings front face.

[0038] The reformer of the resin moldings surface layer which starts invention of this application



according to claim 18 in order to attain the above-mentioned purpose The vacuum housing C1 in which sealing for putting the organic compound which has the resin and compatibility of the resin moldings which has sublimability and is covered on a saturation sublimation pressure condition is possible, The vacuum housing J1 in which sealing for putting said resin moldings on the saturation sublimation pressure condition of said organic compound is possible, The connecting piping which makes a vacuum housing C1 and a vacuum housing J1 connect mutually, and the breaker style of said connecting piping, The exhaust air system which adjusts independently the pressure in a vacuum housing C1, and the exhaust air system which adjusts independently the pressure in a vacuum housing J1, After said organic compound sublimates and the steam of an organic compound adheres to said resin moldings front face, said organic compound is further characterized by establishing the heating means for permeating and distributing into said resin moldings.

[0039] The reformer of the resin moldings surface layer which starts invention of this application according to claim 19 in order to attain the above-mentioned purpose is a reformer of claim 16, claim 17, or a resin surface layer according to claim 18, and is characterized by establishing the device for agitating said powder-like resin moldings.

[0040] The reformer of the resin moldings surface layer which starts invention of this application according to claim 20 in order to attain the above-mentioned purpose is a reformer of claim 16, claim 17, or a resin surface layer according to claim 18, and is characterized by establishing the device for rolling round said resin moldings of the gestalt chosen from the shape of fibrous, the shape of a fiber, and a film from a supply side reel to a recipient reel under a reduced pressure condition.

[0041] The coloring equipment of the resin moldings surface layer which starts invention of this application according to claim 21 in order to attain the above-mentioned purpose The container in which sealing for putting the coloring matter which has the resin and compatibility of the resin moldings which has sublimability and is colored, and said resin moldings on the saturation sublimation pressure condition of said coloring matter is possible, After said coloring matter sublimates with the exhaust air system for adjusting the pressure of the container in which said sealing is possible and the steam of coloring matter adheres to said resin moldings front face, said coloring matter is further characterized by establishing the heating means for permeating and distributing into said resin moldings.

[0042] The coloring equipment of the resin moldings surface layer which starts invention of this application according to claim 22 in order to attain the above-mentioned purpose is coloring equipment of a resin moldings surface layer according to claim 21, is at least one mode chosen from the groups which consist of the five above-mentioned modes, and is further characterized by to form the source substrate of sublimation for being held so that said coloring matter may adhere to said resin moldings front face.

[0043] The coloring equipment of the resin moldings surface layer which starts invention of this application according to claim 23 in order to attain the above-mentioned purpose The vacuum housing C1 in which sealing for putting the coloring matter which has the resin and compatibility of the resin moldings which has sublimability and is colored on a saturation sublimation pressure condition is possible, The vacuum housing J1 in which sealing for putting said resin moldings on the saturation sublimation pressure condition of said coloring matter is possible, The connecting piping which makes a vacuum housing C1 and a vacuum housing J1 connect mutually, and the breaker style of said connecting piping, The exhaust air system which adjusts independently the pressure in a vacuum housing C1, and the exhaust air system which adjusts independently the pressure in a vacuum housing J1, After said coloring matter sublimates and the steam of coloring matter adheres to said resin moldings front face, said coloring matter is further characterized by establishing the heating means for permeating and distributing into said resin moldings.

[0044] The coloring equipment of the resin moldings surface layer which starts invention of this application according to claim 24 in order to attain the above-mentioned purpose is claim 21, claim 22, or coloring equipment of a resin surface layer according to claim 23, and is characterized by establishing the device for agitating said powder-like resin moldings.

[0045] The coloring equipment of the resin moldings surface layer which starts invention of this application according to claim 25 in order to attain the above-mentioned purpose is claim 21, claim 22, or coloring equipment of a resin surface layer according to claim 23, and is characterized by to



establish the device for rolling round said resin moldings of the gestalt chosen from the shape of fibrous, the shape of a fiber, and a film from a supply side reel to a recipient reel under a reduced pressure condition.

[0046] The resin moldings applied to invention of this application according to claim 26 in order to attain the above-mentioned purpose is characterized by carrying out reforming of the surface layer by the reforming approach of claim 1, claim 2, claim 3, claim 4, claim 5, claim 6, claim 7, claim 8, claim 9, claim 10, claim 11, or a resin surface layer according to claim 12.

[0047] The resin moldings applied to invention of this application according to claim 27 in order to attain the above-mentioned purpose is characterized by carrying out reforming of the surface layer by the reforming approach of a resin surface layer according to claim 13.

[0048] The resin moldings applied to invention of this application according to claim 28 in order to attain the above-mentioned purpose is characterized by coloring a surface layer by the coloring approach of a resin surface layer according to claim 14.

[0049] The resin moldings applied to invention of this application according to claim 29 in order to attain the above-mentioned purpose is characterized by coloring a surface layer by the coloring approach of a resin surface layer according to claim 15.

[0050] The plastic lens applied to invention of this application according to claim 30 in order to attain the above-mentioned purpose is characterized by carrying out reforming of the surface layer by the reforming approach of claim 1, claim 2, claim 3, claim 4, claim 5, claim 6, claim 7, claim 8, claim 9, claim 10, claim 11, or a resin surface layer according to claim 12.

[0051] The plastic lens applied to invention of this application according to claim 31 in order to attain the above-mentioned purpose is characterized by coloring a surface layer by the coloring approach of a resin surface layer according to claim 14.

[0052] The resin coat lens applied to invention of this application according to claim 32 in order to attain the above-mentioned purpose is characterized by carrying out reforming of the resin surface layer by the reforming approach of claim 1, claim 2, claim 3, claim 4, claim 5, claim 6, claim 7, claim 8, claim 9, claim 10, claim 11, or a resin surface layer according to claim 12.

[0053] The resin coat lens applied to invention of this application according to claim 33 in order to attain the above-mentioned purpose is characterized by coloring a resin surface layer by the coloring approach of a resin surface layer according to claim 14.

[0054] The plastic film applied to invention of this application according to claim 34 in order to attain the above-mentioned purpose is characterized by carrying out reforming of the surface layer by the reforming approach of claim 1, claim 2, claim 3, claim 4, claim 5, claim 6, claim 7, claim 8, claim 9, claim 10, claim 11, or a resin surface layer according to claim 12.

[0055] The plastic film applied to invention of this application according to claim 35 in order to attain the above-mentioned purpose is characterized by coloring a surface layer by the coloring approach of a resin surface layer according to claim 14.

[0056] The fiber which starts invention of this application according to claim 36 in order to attain the above-mentioned purpose is characterized by carrying out reforming of the surface layer by the reforming approach of claim 1, claim 2, claim 3, claim 4, claim 5, claim 6, claim 7, claim 8, claim 9, claim 10, claim 11, or a resin surface layer according to claim 12.

[0057] The fiber which starts invention of this application according to claim 37 in order to attain the above-mentioned purpose is characterized by coloring a surface layer by the coloring approach of a resin surface layer according to claim 14.

[0058] The plastic optical fiber applied to invention of this application according to claim 38 in order to attain the above-mentioned purpose is characterized by carrying out reforming of the surface layer by the reforming approach of claim 1, claim 2, claim 3, claim 4, claim 5, claim 6, claim 7, claim 8, claim 9, claim 10, claim 11, or a resin surface layer according to claim 12.

[0059] The plastic optical fiber applied to invention of this application according to claim 39 in order to attain the above-mentioned purpose is characterized by coloring a surface layer by the coloring approach of a resin surface layer according to claim 14.

[0060] The resin moldings applied to invention of this application according to claim 40 in order to attain the above-mentioned purpose Claim 1, claim 2, claim 3, claim 4, claim 5, claim 6, claim 7, claim 8, claim 9, claim 10, claim 11, Or it is characterized by giving a firefly luminescence function

to a surface layer by surface layer reforming using the fluorochrome which has the resin and compatibility of the reforming approach of a resin surface layer according to claim 12, and the resin moldings which has sublimability and is covered.

[0061] The resin moldings applied to invention of this application according to claim 41 in order to attain the above-mentioned purpose Claim 1, claim 2, claim 3, claim 4, claim 5, claim 6, claim 7, claim 8, claim 9, claim 10, claim 11, Or it is characterized by giving a photochromic function to a surface layer by surface layer reforming using the photochromic coloring matter which has the resin and compatibility of the reforming approach of a resin surface layer according to claim 12, and the resin moldings which has sublimability and is covered.

[0062] The resin moldings applied to invention of this application according to claim 42 in order to attain the above-mentioned purpose Claim 1, claim 2, claim 3, claim 4, claim 5, claim 6, claim 7, claim 8, claim 9, claim 10, claim 11, By or surface layer reforming using the organometallic compound which has the resin and compatibility of the reforming approach of a resin surface layer according to claim 12, and the resin moldings which has sublimability and is covered It is characterized by giving an X-ray, an electron ray, and/or a radiation absorption function to a surface layer.

[0063] The resin moldings applied to invention of this application according to claim 43 in order to attain the above-mentioned purpose Claim 1, claim 2, claim 3, claim 4, claim 5, claim 6, claim 7, claim 8, claim 9, claim 10, claim 11, Or it is characterized by giving an antibacterial mildewproofing function to a surface layer by surface layer reforming using the reforming approach of a resin surface layer according to claim 12, and the anti-fungus and mildewproofing agent which has the resin and compatibility of the resin moldings which has sublimability and is covered.

[0064] The resin moldings applied to invention of this application according to claim 44 in order to attain the above-mentioned purpose Claim 1, claim 2, claim 3, claim 4, claim 5, claim 6, claim 7, claim 8, claim 9, claim 10, claim 11, Or it is characterized by giving a pharmacological activity function to a surface layer by surface layer reforming using the pharmacological activity organic compound which has the resin and compatibility of the reforming approach of a resin surface layer according to claim 12, and the resin moldings which has sublimability and is covered.

[0065] The resin moldings applied to invention of this application according to claim 45 in order to attain the above-mentioned purpose Claim 1, claim 2, claim 3, claim 4, claim 5, claim 6, claim 7, claim 8, claim 9, claim 10, claim 11, Or it has the reforming approach of a resin surface layer according to claim 12, and the resin and compatibility of a resin moldings which have sublimability and are covered, and is characterized by giving the function as agricultural chemicals to a surface layer by surface layer reforming using the organic compound in which bioactive is shown to animals and plants.

[0066]

[Embodiment of the Invention] Hereafter, it explains in full detail about the gestalt of suitable operation of this invention.

[0067] [Reforming of a resin surface layer] In this invention with reforming of a resin moldings surface layer The physical properties of the surface layer part in Mr. Fukashi predetermined [ the front face of a resin moldings to ] For example, a consistency, a degree of hardness, impact strength, an elastic modulus, acoustic velocity, a dielectric constant, permeability, Electrical conductivity, surface electrical resistance, a volume resistivity, a photoconductivity, static electricity electrification ranking, electrification nature, It says changing light transmittance, the rate of a light reflex, polarizability, a refractive index, secondary light nonlinear susceptibility, 3rd light nonlinear susceptibility, a nonlinear refractive index, a hydrophilic property, a contact angle with water, hydrophobicity, oleophilic, gas permeability, water absorption, etc. in a resin independent case. Moreover, compared with a resin independent case, the case where the photolysis reaction by oxidative degradation, the pyrolysis reaction, ultraviolet rays, and/or the visible ray etc. is controlled is included by reforming a resin moldings surface layer. Moreover, compared with a resin independent case, the case where functions, such as fluorescence, phosphorescence, photochromic one, and a photorefractive effect, are given to a resin moldings surface layer is included by reforming a resin moldings surface layer. Furthermore, the case where a bioactive function and/or pharmacological activity functions, such as an antibacterial action and a mildewproofing operation,

are given to a resin moldings surface layer is included by reforming a resin moldings surface layer. [0068] Here, the thickness of the surface layer by which reforming is carried out, i.e., the depth from a front face, makes an upper limit the case where reforming of the whole resin moldings is carried out by making level of an atom or one molecule into a minimum.

[0069] [Coloring of a resin surface layer] If the light transmittance, the rate of a light reflex, and/or refractive index of a surface layer change by having carried out reforming of the resin moldings surface layer, the color on appearance will change with a reforming front. That is, it can be considered that coloring of a resin surface layer is one sort of surface treatment. If the sublimability organic compound used in order to change the physical properties of a resin surface layer is colored, the color of a resin surface layer will turn into a color which added the colored organic compound to the color of resin original.

[0070] In this invention, it shall call it "coloring" to reform a resin surface layer for the purpose of changing the color on the appearance of a resin moldings.

[0071] [Resin moldings] Reforming and the coloring approach of the resin moldings surface layer of this invention are characterized by permeating and distributing said organic compound which put the organic compound which has the resin and compatibility of the resin moldings which has sublimability and is covered on the saturation sublimation pressure condition of said organic compound, and said organic compound steam was made to adhere to homogeneity on said resin moldings front face, and adhered from said resin moldings front face to the interior.

[0072] Here, a resin moldings may be the gestalt of arbitration. A resin material specifically The letter of a block, a globular shape, hemispherical, a pellet type, cylindrical, The shape of the shape of a pipe, and a tube, a rectangular parallelepiped, a cube, and prism, a cone, a triangular pyramid, The shape of a thin film established on substrates, such as the shape of the shape of the shape of a square drill and a lens, plate-like, and a sheet, and a film, and a thin film, and glass, The plastics moldings to which the configuration of arbitration was given by the shaping approaches, such as a thing fabricated in the gestalt of the shape of a fiber, fiber, a plastic optical fiber, etc. or an injection-molding method, can be used. The fibrous resin moldings was processed further and gestalten, such as the shape of the shape of the shape of yarn by which spinning was carried out, and textiles, and a nonwoven fabric, may be taken.

[0073] Moreover, there is especially no limit about the size of a resin moldings. That is, \*\* may be the powder and/or impalpable powder of several nanometers resin from hundreds of micrometers outside a particle.

[0074] Moreover, you may fabricate combining two or more kinds of resin. For example, the resin moldings of the structure of the shape of a sheet which used a sublimability organic compound and affinitive resin as the 1st layer of a front face, and made the laminated structure two or more kinds of other resin under this 1st layer can be used. Furthermore, the front face of the structure which consists of the quality of the materials other than resin may be covered by the film of a sublimability organic compound and affinitive resin. For example, what carried out the coat of the thin film of affinitive resin to the sublimability organic compound can also be used for the front face of a glass lens or a plastic lens.

[0075] [Resin] In this invention, the polymer of an organic compound, an organic high molecular compound, plastics, a polymer, and oligomer are included with "resin." It may be thermoplasticity or you may be thermosetting. As the example, ketone resin, norbornene resin, polystyrene, Pori (alpha methyl styrene), the poly indene, Pori (4-methyl-1-pentene), Polyvinyl pyridine, polyacetal, a polyvinyl formal, a polyvinyl acetal, A polyvinyl butyral, polyvinyl acetate, Pori propionic-acid vinyl, Polyvinyl alcohol, polyethylene, polypropylene, polybutadiene, The poly methyl pentene, a polyvinyl chloride, a chlorination polyvinyl chloride, chlorinated polyethylene, Chlorination polypropylene, a polyvinylidene chloride, polytetrafluoroethylene, Polychlorotrifluoroethylene resin, polyvinylidene fluoride, polyvinyl methyl ether, Polyvinyl ethyl ether, polyvinyl benzyl ether, a polyvinyl methyl ketone, Pori (N-vinylcarbazole), poly(N-vinylpyrrolidone), Polymethylacrylate, polyacrylic acid ethyl, polyacrylic acid, a polyacrylonitrile, A polymethyl methacrylate, polymethacrylic acid ethyl, polymethacrylic acid butyl, Polymethacrylic acid benzyl, polymethacrylic acid cyclohexyl, polymethacrylic acid, A polymethacrylic acid amide, the poly methacrylonitrile, the poly acetaldehyde, The poly trichloroacetic aldehyde, polyethylene oxide,

polypropylene oxide, Polyethylene terephthalate, polybutylene terephthalate, and polycarbonates (bisphenols + carbonic acid) The poly amine, polyether sulphone, polyphenylene sulfide, Pori (diethylene-glycol bisallyl carbonate), 6-nylon, 6 and 6-nylon, 12-nylon, 6, 12-nylon, Pori aspartic-acid ethyl, Polyglutamic acid ethyl, the poly lysine, polyproline, Pori (gamma-benzyl-L-glutamate), Methyl cellulose, ethyl cellulose, benzyl cellulose, hydroxyethyl cellulose, Hydroxypropylcellulose, an acetyl cellulose, cellulose triacetate, Cellulose butyrate, alkyd resin (phthalic anhydride + glycerol), Fatty-acid modified alkyd resin (fatty-acid + phthalic anhydride + glycerol), an unsaturated polyester resin (maleic-anhydride + phthalic anhydride + propylene glycol), An epoxy resin (bisphenols + epichlorohydrin), an epoxy resin (cresol novolak + epichlorohydrin), Polyurethane resin, phenol resin, a urea-resin, melamine resin, xylene resin, Organic polysilane, such as resin, such as a toluene resin, furan resin, guanamine resin, and diallyl phthalate resin, and Pori (phenyl methylsilane), the organic poly germane, and these copolymerization and copolycondensation objects are mentioned. As a copolymer, plastics, such as an acrylonitrile + styrene (AS resin), acrylonitrile + acrylate + styrene (AAS resin), acrylonitrile + ethylene + styrene (AES resin), acrylonitrile + butadiene + styrene (ABS plastics), acrylonitrile + chlorinated polyethylene + styrene (ACS resin), methyl methacrylate + butadiene + styrene (MBS resin), and ethylene-vinyl chloride copolymer, an ethylene-vinyl acetate copolymer, and an ethylene vinyl alcohol copolymer, can be mentioned. Moreover, a carbon disulfide, carbon tetrafluoride, ethylbenzene, perfluoro benzene, a perfluoro cyclohexane, or trimethylchlorosilane can use in usual the high molecular compound which carried out the plasma polymerization of the compound without polymerization nature, and obtained it.

[0076] [Sublimability organic compound] Sublimation is the process in which a solid-state changes to a direct gas, without going via the liquid which is an intermediate phase, and if it is below the temperature of the triple point, it is a universal phenomenon which happens about all solid-states. However, for example, when it heats beyond ordinary temperature, organic compounds, such as ionic crystals, such as an azo compound of large molecular weight and poly methine coloring matter, will not be based on a pressure, but will be pyrolyzed, without showing the melting point. It can be said that the triple point does not exist as a matter of fact, and is not sublimated to such matter. In order to distinguish from such matter, suppose that the organic compound which can be sublimated is called a "sublimability organic compound", without being accompanied by the pyrolysis.

[0077] It can consider as the example of a sublimability organic compound, for example, the following compound groups can be mentioned.

[0078] As sublimability and a colorless organic compound, phenol derivatives, such as - methylenebis (4-methyl-6-tert-butylphenol), and 2, 6-G tert-butyl-p-cresol, butyl-ized hydroxyanisole, 2, 6-G tert-butyl-4-ethylphenol, 2, and 2', 2'-methylenebis (4-ethyl-6-tert-butylphenol), can be used. These compounds are known as an antioxidant of plastics and can strengthen an antioxidizing operation of a surface layer by reforming a resin surface layer using these. Moreover, it can use also for the purpose which changes the consistency of a resin surface layer, a degree of hardness, impact strength, an elastic modulus, acoustic velocity, a dielectric constant, static electricity electrification ranking, electrification nature, a refractive index, etc., without changing the color of a resin moldings.

[0079] As an organic compound of sublimability and colorlessness thru/or light yellow, a phenyl salicylate, Salicylic-acid p-tert-butylphenyl, salicylic-acid p-octyl phenyl, 2, 4-dihydroxy benzophenone, 2-hydroxy-4-methoxybenzophenone, 2, 2'-dihydroxy-4-methoxybenzophenone, 2, 2'-dihydroxy -4, a 4'-dimethoxy benzophenone, 2-(2'- hydroxy-5'-methylphenyl) benzotriazol, 2-(2'-hydroxy-5'-tert-butylphenyl) benzotriazol, 2-(2'- hydroxy-3', 5'-G tert-butylphenyl) benzotriazol, 2-(2'- hydroxy-3'-tert-butyl-5-methylphenyl)-5-chlorobenzo triazole, 2-(2'- hydroxy-3', 5'-G tert-butylphenyl)-5-chlorobenzo triazole, 2-[(2'- hydroxy-3'-(3", 4", 5"6"-tetrahydro phthalimidomethyl)-5'-methylphenyl] benzotriazol --) 2-(2'- hydroxy-5'-meta-acryloxy phenyl)-2H-benzotriazol, ethyl-2-cyano - 3 and 3'-diphenyl acrylate etc. can be mentioned. These compounds are known as an ultraviolet ray absorbent for plastics, and can strengthen an ultraviolet absorption operation of a surface layer by reforming a resin surface layer using these. Moreover, it can use also for the purpose which changes the consistency of a resin surface layer, a degree of hardness, impact

strength, an elastic modulus, acoustic velocity, a dielectric constant, static electricity electrification ranking, electrification nature, a refractive index, etc., without changing the color of a resin moldings.

[0080] It is the organic molecular compound which forms the single crystal in which a secondary nonlinear optical effect is shown. As an organic compound of sublimability A urea and its derivative, meta nitroaniline, 2-methyl-4-nitroaniline, Benzene derivatives, such as 2-(N and N-dimethylamino)-5-nitro acetanilide, N, and N'-screw (4-nitrophenyl) methane diamine, Stilbene derivatives, such as biphenyl derivatives, such as - nitro biphenyl, and a 4-methoxy-4'-methoxy-4'-nitro stilbene, 4-nitro-3-picoline = chalcone derivatives, such as pyridine derivatives, such as N-oxide, 2', 4, and a 4'-trimethoxy chalcone, a thienyl chalcone derivative, etc. can be mentioned. Without changing the color of resin surface layer original, since it is colorlessness thru/or yellow, these organic compounds can be used in order to change the consistency of a resin surface layer, a degree of hardness, impact strength, an elastic modulus, acoustic velocity, a dielectric constant, static electricity electrification ranking, electrification nature, a refractive index, 3rd light nonlinear susceptibility, a nonlinear refractive index, a photorefractive effect property, etc.

[0081] Light absorption can be shown in the wavelength band of ultraviolet a visible ray - a near infrared ray, and azo dye, porphyrin coloring matter, phthalocyanine dye, triphenylmethane color system coloring matter, naphthoquinone coloring matter, an anthraquinone pigment, naphthalene tetracarboxylic acid diimide coloring matter, perylene tetracarboxylic acid diimide coloring matter, etc. can be mentioned as an example of the organic compound (organic coloring matter) of sublimability. A resin moldings surface resin layer can be colored by using these coloring matter. Moreover, when these coloring matter presents fluorescence, the function which presents fluorescence to the surface layer of a resin moldings can be given.

[0082] As an example of sublimability azo dye, an azobenzene, 4-dimethylaminoazo benzene, a 4-dimethylamino-3'-nitro azobenzene, 4-dimethylamino-4'-nitro azobenzene and 4-dimethylamino-3-methyl-3'-nitro azobenzene, and 4-dimethylamino-3-methyl-4'-nitro azobenzene, 4-nitro azobenzene, etc. can be mentioned, for example.

[0083] As an example of porphyrin coloring matter, a porphyrin, a tetra-phenyl porphyrin, etc. can be mentioned, for example.

[0084] As an example of phthalocyanine dye, a phthalocyanine, a copper phthalocyanine, a cobalt phthalocyanine, a nickel phthalocyanine, a chloro aluminum phthalocyanine, etc. can be mentioned, for example.

[0085] As an example of triphenylmethane color system coloring matter, crystal violet lactone, 3-diethylamino-6-methyl-7-chlorofluoran, 3-diethylamino-7-methylamino fluoran, 3-diethylamino-7-phenylamino fluoran, etc. can be mentioned, for example.

[0086] As an example of naphthoquinone coloring matter, 1,4-naphthoquinone, a 2, 3-dichloro-1, 4-naphthoquinone, a 5-amino-2, 3-dichloro-1, 4-naphthoquinone, the 8-phenylamino 5-amino -2, 3-dicyano-1,4-naphthoquinone, etc. can be mentioned, for example.

[0087] As an example of an anthraquinone pigment, anthraquinone, 1-aminoanthraquinone, 1,4-dihydroxyanthraquinone, etc. can be mentioned, for example.

[0088] As an example of naphthalene tetracarboxylic acid diimide coloring matter, it is 1, 4, 5, 8-naphthalene tetracarboxylic acid diimide, N, and N'-dimethyl, for example. - 1, 4, 5, and 8-naphthalene tetracarboxylic acid diimide etc. can be mentioned.

[0089] As an example of perylene tetracarboxylic acid diimide coloring matter, it is 3, 4, 9, 10-perylene tetracarboxylic acid diimide, N, and N'-G tert-butyl, for example. - 3, 4, 9, 10-perylene tetracarboxylic acid diimide, etc. can be mentioned.

[0090] A photochromic phenomenon as a lifting, sublimability, and a crystalline organic compound 6-BUROMO - 1', 3' - dihydro-1', 3', 3'-trimethyl-8-nitro SUPIRO [2H-1-benzopyran -2 and 2'-(2H)-Indore], 5-chloro -1, 3-dihydro - 1, 3, and 3-trimethyl SUPIRO [2H-Indore -2 and 3'-(3H) [2 and 1-naphth b] [1, 4] oxazine], 5-chloro -1, 3-dihydro - 1, 3, and 3-trimethyl SUPIRO [2H-Indore -2 and 3'-(3H) [9 and 10-naphth b] [1, 4] oxazine], 6, 8-dibromo - 1', 3' - dihydro-1', 3', 3'-trimethyl SUPIRO [2H-1-benzopyran -2 and 2'-(2H)-Indore], 1', 3' - dihydro-1', 3', 3'-trimethyl-6-nitro SUPIRO [2H-1-benzopyran -2 and 2'-(2H)-Indore], 1', 3' - dihydro-5'-methoxy-1', 3', 3'-trimethyl-6-nitro SUPIRO [2H-1-benzopyran -2 and 2'-(2H)-Indore], 1', 3' - dihydro-8-methoxy-1', 3', 3'-

trimethyl-6-nitro SUPIRO [2H-1-benzopyran -2 and 2'-(2H)-Indore], 1, 3-dihydro - 1, 3, and 3-trimethyl SUPIRO [2H-Indore -2 and 3'-[3H] [2 and 1-naphth b] [1, 4] oxazine], 1, 3-dihydro - 1, 3, and 3-trimethyl SUPIRO [2H-Indore -2 and 3'-[3H] [9 and 10-FENANSURO b] [1, 4] oxazine], 1, 3-dihydro - 1, 3, and 3-trimethyl SUPIRO [2H-Indore -2 and a 3'-[3H] [2 and 1-naphth b] pyran], SUPIRO pyrans, such as 1, the 3-dihydro-5-methoxies 1 and 3, and 3-trimethyl SUPIRO [2H-Indore -2 and a 3'-[3H] [2 and 1-naphth b] pyran]; 2, a 5-dimethyl-3-furil ethylidenesuccinic acid anhydride, Fulgides, such as a 2 and 5-dimethyl-3-FURIRUIRO propylidene succinic-acid anhydride; 2, 3-screw (2, 4, 5-trimethyl-3-thienyl) maleic-acid anhydride, Diaryl ethenes, such as 2, 3-screw (2, 4, 5-trimethyl-3-thienyl) maleimide, cis-1, 2-dicyano -1, and 2-screw (2, 4, 5-trimethyl-3-thienyl) ethene, can be mentioned. A photochromic property can be given to the surface layer of a resin moldings by reforming a resin surface layer using these photochromic coloring matter.

[0091] As an organometallic compound of sublimability, metallocenes, such as titanocene, BANAJINOSEN, clo MOSEN, comics NOSEN, a ferrocene, Cobalt Seng, nickelocene, and RUTENOSEN, can be mentioned. By reforming a resin surface layer using the organometallic compound of these sublimability, the permeability property of an X-ray or an electron ray is changeable.

[0092] Moreover, since BANAJINOSEN, clo MOSEN, comics NOSEN, Cobalt Seng, nickelocene, etc. have the magnetic moment, a magnetic property is changeable by reforming a resin surface layer using the organometallic compound of these sublimability.

[0093] As an organic compound of sublimability, a dichlorophenol, trichlorophenol, tetrachlorophenol, pentachlorophenol, p-chloro-m-xylenol, p-chloro-m-cresol, 4-chloro-2-phenylphenol, 2, 4 and 5, 6-tetra-chloro isophthalonitrile, 10, and 10'-oxy-screw phenoxy arsine, N-(TORIKUORO methylthio) phthalimide, N-(fluoro dichloro methylthio) phthalimide, etc. can be mentioned. These compounds are known as the preservation from decay and an antifungal agent for plastics, and can give an antibacterial mildewproofing function to a resin surface layer by reforming a resin surface layer using these. By using the reforming approach of the resin moldings surface layer of this invention, it becomes possible to stop the amount of preservation from decay and the antifungal agent used to necessary minimum compared with the case where scour preservation from decay and an antifungal agent to the whole plastics, and it is crowded in it.

[0094] The function as physic and/or agricultural chemicals can be given to a resin surface layer by similarly reforming a resin surface layer as an organic compound of sublimability using an organic compound with pharmacological activity. for example, the thing for which L-menthol (melting point of 43 degrees C) is used -- an analgesic action -- moreover, a strong alignment operation can be given as a function of the surface layer of a resin moldings, for example, plastic film, by using camphor (melting point of 179 degrees C). Similarly, agricultural-chemicals functions, such as for example, a weeding-out function, a insect-killing function, a noxious insect \*\*\*\* function, a plant growth promotion function, and a plant growth inhibitor, can be given to the surface layer of a sheet plastic.

[0095] As sublimability and a crystalline organic compound, 3,4-dimethoxybenzaldehyde (melting point of 40 degrees C), a 3-oxy--2-methyl-4-pyrone (melting point of 161 degrees C), etc. can be mentioned. It has these compounds as perfume, they are, and can give the function to generate a scent strong against a resin surface layer, by reforming a resin surface layer using these.

[0096]

[Example] Hereafter, an example is shown and the approach of this invention is explained in more detail.

[0097] [Example 1] The glass tube 10 which closed the end as shown in drawing 1 (For example, the outer diameter of 15mm, the bore of 12mm, die length of 200mm) Inside As an organic compound 20 which has the resin and compatibility of the resin moldings which has sublimability and is covered, 5mg of crystals of cis-1, 2-dicyano -1, and 2-screw (2, 4, 5-trimethyl-3-thienyl) ethene (the melting point of 121 degrees C; Tokyo formation product made from industry), 5-6 pellets (the outer diameter of about 2.5mm and die length of 2.5mm -- cylindrical) of the bisphenol A polycarbonate (made in Aldrich Chemical, Inc.) were installed as a resin moldings. Then, it exhausted until it connected the other end of a glass tube 10 to evacuation equipment 50 and the pressure in tubing was set to 10 - 5 or less Pa under the room temperature, as shown in drawing 2 (A). Subsequently, as

shown in drawing 2 R> 2 (B), the melting sealed tube of the part near the end connection of said glass tube 10 was carried out by the burner 60 for the glass tube sealed tubes, and said organic compound and said resin pellet were sealed in the glass sealed tube 11 which stopped both ends. [0098] Next, it heated, having installed said glass sealed tube 11 in the thermostat 70, having covered said glass sealed tube 11 whole, having made into the minimum temperature (in the case of the above-mentioned compound 110 degrees C) sublimated without said sublimability organic compound pyrolyzing, and carrying out temperature control to a precision by making highest temperature into an upper limit among the temperature with which the following conditions are filled, as shown in drawing 3 .

[0099] (a) the temperature which does not exceed the melting initiation temperature of said sublimability organic compound, and (b) -- the glass transition temperature (in the case of a polycarbonate about 150 degrees C) of said resin, and (c) -- the heat deformation initiation temperature of said resin, and (d) -- the melting initiation temperature of said resin, and (e) -- the temperature which does not exceed the decomposition initiation temperature of said resin.

[0100] In addition, to enforce resin surface layer reforming and/or the coloring approach of this invention, without losing the fine structure in the surface smooth nature and the front face of a resin moldings, it is necessary to carry out temperature control so that heat deformation initiation temperature of said resin may not be exceeded.

[0101] In this example, the internal temperature of a thermostat 70 was set as 110 degrees C, and it maintained in the precision of  $\pm 0.1$  degrees C to laying temperature for 24 hours. Then, the temperature of a thermostat 70 was gradually reduced over 9 hours to 25 degrees C. In addition, when said glass sealed tube 11 is taken out out of a thermostat and it cools quickly, the steam of said sublimability organic compound touches the wall of said cooled glass sealed tube 11, and condenses, it deposits as a crystal, and there is a possibility that a sublimability organic compound may not be permeated and distributed by specified quantity homogeneity in a resin surface layer here.

[0102] In this example, it cooled to the room temperature gradually and the cooling aforementioned glass sealed tube 11 was taken out, the glass sealed tube 11 was cut and the pellet of the polycarbonate which said sublimability organic compound permeated and distributed was taken out to the surface layer. This pellet was cut into round slices by the cutter, it observed with the optical microscope, and the cross-section photograph as shown in drawing 10 was taken. One graduation of the scale inserted into drawing 10 is 10 micrometers. A depth of about 90 micrometers is covered from the front face of the pellet of the poly car boat so that clearly from drawing 10 , said sublimability organic compound permeates and distributes at a surface layer, and a surface layer is known by reforming and having been colored.

[0103] Furthermore, by measurement of the light absorption spectrum of the obtained resin surface layer, optical microscope observation (usually visual field), polarization microscope observation, scanning electron microscope observation of said resin pellet front face, and transmission electron microscope observation of said resin pellet cross section, inside said resin pellet, it dissolution-ized and molecular dispersion, i.e., reforming and coloring of a surface layer are done, was checked for said sublimability organic compound. In addition, the crystal of said sublimability organic compound was not observed the front face and inside the resin pellet. [ which were obtained ]

[0104] It was observed by osmosis of said sublimability organic compound, cis-1, 2-dicyano -1, and 2-screw (2, 4, 5-trimethyl-3-thienyl) ethene that reforming and the colored polycarbonate surface layer change with the exposures of ultraviolet rays to yellow at red by the exposure of the visible ray and/or infrared radiation which omitted ultraviolet rays. That is, it was checked that the photochromic function had been given to the resin surface layer.

[0105] Drawing 3 shows the simplest operation gestalt of resin surface layer reforming of this invention, and/or coloring equipment. That is, in the glass tube 11 which stopped both ends, the organic compound 20 which there are the resin and compatibility of a resin moldings (resin pellet 30) and said resin moldings, and has sublimability is arranged. Within this glass tube 11, said organic compound is put on a saturation sublimation pressure condition. Moreover, a thermostat 70 is a heating means for said organic compound sublimating, and the steam of said organic compound adhering to said resin moldings front face, and permeating and distributing said organic compound in said resin moldings further.



[0106] [the example 1 of a comparison] -- as the organic compound 20 which has the resin and compatibility of the resin moldings which has sublimability and is covered in the glass tube 10 (for example, the outer diameter of 15mm, the bore of 12mm, die length of 200mm) which closed the end -- for example Heating and annealing of the glass sealed tube 11 were performed like the example 1 except having put in only the crystal of cis-1, 2-dicyano -1, and 2-screw (2, 4, 5-trimethyl-3-thienyl) ethene. The steam of said sublimability organic compound sublimated and generated at the time of heating did not adhere to return and the glass wall of a glass tube 11 on the front face of the original crystal at the time of annealing. In addition, when the glass sealed tube 11 in a heating condition was taken out from the thermostat and it cooled quickly, the steam of said sublimability organic compound touched the wall of said cooled glass sealed tube 11, condensed, deposited as a crystal, and adhered to the wall of said glass sealed tube 11. Thus, since a crystal deposits to a glass sealed tube wall when it quenches, it turns out that sublimation advanced and the steam of said sublimability organic compound is full in the glass sealed tube with heating.

[0107] [an example 2] -- polymethyl-methacrylate (PMMA): -- 2.0g -- acetone: -- it dissolved in 200ml. The resin powder which deposited while stirring this solution into n-hexane:800ml was carried out the \*\* exception. After washing this resin powder by n-hexane, it was made to dry under reduced pressure, and subsequently it ground. Heating was continued for the obtained resin powder for two days at 100 degrees C under the ultra-high vacuum of less than 10 - 5Pa, and volatile components, such as a residual solvent, were removed completely. In 100mg of this powder, it is a glass substrate (the thickness of 0.14mm, and width of face of 10mm). It inserts with a spacer with a thickness of 100 micrometers between die length of 20mm, and aluminum foil (20 micrometers in thickness, width of face of 10mm, die length of 20mm). Furthermore, the glass plate of one more sheet was piled up on aluminum foil, it heated at 150 degrees C under the vacuum, and the film (about 100 micrometers of thickness) of PMMA was produced between a glass substrate/aluminum foil using the approach (vacuum hot pressing) of sticking the glass plate of two sheets by pressure. Subsequently, after cooling enough, aluminum foil was removed and the PMMA thin film 33 formed on the glass substrate 40 was obtained.

[0108] As an organic compound 20 which has the resin and compatibility of the resin moldings which has sublimability and is covered in the glass tube 10 (for example, the outer diameter of 15mm, the bore of 12mm, die length of 200mm) which closed the end 20mg of crystals of cis-1, 2-dicyano -1, and 2-screw (2, 4, 5-trimethyl-3-thienyl) ethene, The glass substrate with which said resin thin film 33 was formed was installed, and it exhausted until it connected the other end of a glass tube 10 to evacuation equipment 50 and the pressure in tubing was set to 10 - 5 or less Pa under the room temperature. Then, the melting sealed tube of the part near the end connection of said glass tube 10 was carried out by the burner 60 for the glass tube sealed tubes, and said organic compound and said resin thin film were sealed in the glass sealed tube 11 which stopped both ends.

[0109] As shown in drawing 4 , said glass sealed tube 11 was installed in the thermostat 70, and said glass sealed tube 11 whole was covered, and it heated in the temperature (in the case of the above-mentioned compound 110 degrees C) sublimated without said sublimability organic compound pyrolyzing, carrying out temperature control to a precision. The temperature of a thermostat 70 was gradually reduced over 9 hours 5 hours after to 25 degrees C.

[0110] Molecular dispersion, i.e., have dissolution-ized, was checked for said sublimability organic compound by the surface layer of said resin thin film 33 covering a depth of about 20 micrometers by measurement of the light absorption spectrum of the obtained resin thin film, optical microscope observation (usually visual field), polarization microscope observation, scanning electron microscope observation of said resin thin film front face, and transmission electron microscope observation of said resin thin film cross section. In addition, the crystal of said sublimability organic compound was not observed the front face and inside the resin thin film. [ which were obtained ] That is, said sublimability organic compound permeates and distributes from the front face of the PMMA resin thin film 33 formed on the glass substrate 40, and a surface layer (20 micrometers in thickness) is known by reforming and having been colored.

[0111] The polycarbonate resin thin film in which reforming was carried out by cis-1, the 2-dicyano -1, and 2-screw (2, 4, 5-trimethyl-3-thienyl) ethene which were produced by this example changes with the exposures of ultraviolet rays to yellow at red by the exposure of the visible ray and/or



infrared radiation which omitted ultraviolet rays. That is, functioning as a photochromic thin film was checked. The visible ray and infrared radiation which cut light with a wavelength of less than 400nm are irradiated for 20 minutes, and 2, 4, 6, and the result of having irradiated for 8 or 10 hours and having measured change of an absorption spectrum are shown for the ultraviolet rays (main wavelength of 366nm) of the black light in what became yellow at drawing 11. the spectrum a visible ray with a wavelength of 400nm or more and 20 minutes after an infrared exposure -- a continuous line shows [ the 2 hour back of a dotted line and UV irradiation / the long chain-line and 4 hour back of said one / the short chain-line and 6 hour back of said one ] the dashed-line and 10-hour back of said one for the two-dot chain line and 8-hour back of said one.

[0112] [Example 3] The glass substrate 40 which has the resin thin film 33 (100 micrometers of thickness) which formed Pori (2-hydroxypropyl methacrylate) (PHPMA) on the glass substrate 40 (for example, the thickness of 0.14mm, width of face of 10mm, die length of 50mm) by the vacuum hot pressing other than the PMMA substrate in an example 2 was produced. And this different kind of resin thin film put in two glass substrates 40 formed respectively in the same glass sealed tube 11, and performed heating and annealing like the example 2 with the organic compound 20 which has the resin and compatibility of the resin moldings which has sublimability and is covered. As a result of spectrum observation, to the PMMA thin film, said sublimability organic compound dissolution-ized like the example 2, and reforming and being colored were checked for the surface layer. On the other hand, the absorption which belongs to said sublimability organic compound was not checked by ultraviolet, visible, and the infrared absorption spectrum of the obtained PHPMA thin film. Although, as for said sublimability organic compound, there is compatibility in PMMA in this result, there is no compatibility in PHPMA, and when there is no compatibility, osmosis and distribution into a resin thin film can be interpreted as not taking place.

[0113] [Example 2 of a comparison] Heating and annealing were performed like the example 2 with the organic compound 20 which has the resin and compatibility of the resin moldings which has sublimability and is covered about the glass sealed tube 11 which put in only the resin thin film 33 (100micro of thickness) which fabricated Pori (2-hydroxypropyl methacrylate) (PHPMA) by vacuum hot pressing on the glass substrate 40 (for example, the thickness of 0.14mm, width of face of 10mm, die length of 50mm). The absorption which belongs to said sublimability organic compound was not checked by the absorption spectrum of the obtained PHPMA thin film as a result of spectrum observation.

[0114] As mentioned above, the thing said sublimability organic compound sublimates into the decompressed glass sealed tube at the time of heating, and a steam is [ thing ] full in a glass tube from observation of examples 1, 2, and 3 and the examples 1 and 2 of a comparison, If a heating condition will be maintained without [ that a vacuum evaporatio process advances and ] cooling if the steam is cooled, and said sublimability organic compound and affinitive resin moldings (pellet and resin thin film) are placed there In the resin surface layer, said sublimability organic compound dissolution[ molecular dispersion and ]-ized, and reforming and/or being colored were checked for the surface layer. Although said sublimability organic compound was once sublimated on the other hand when said sublimability organic compound and affinitive resin moldings did not exist, returning [ said sublimability organic compound steam ]-to crystal front face \*\* was checked by annealing.

[0115] Here, about the compatibility of said sublimability organic compound and resin, he can understand as "existence of stabilization by solvation energy." That is, resin is acting here as a "solvent" in the case of the "medium" and solution to said sublimability organic compound. In the case where the compatibility of said sublimability organic compound and resin is not accepted, resin is acting as "a medium of solubility zero." In this case, since it is "nothing [ the stabilization by solvation energy ]", said sublimability organic compound steam cannot permeate and distribute in resin. Therefore, if it cools slowly after heating to a maximum-vapor-tension condition, as for the steam of said sublimability organic compound, it is thermodynamically most stable to return to a crystal front face again and to crystallize. On the other hand, when "there is stabilization by solvation energy", said sublimability organic compound steam which arrived at the resin front face is evaporated again, and the direction dissolution-ized into resin stabilizes it rather than returning to a crystal front face. When it puts in another way and there "there is stabilization by solvation energy",

"the dissolution" from a crystal front face to the inside of resin advances through the vacuum. In addition, based on rules of thumb, such as the similarity of a molecule substructure, and a soluble parameter, it is necessary to search by trial and error like the case where it looks for the solvent suitable for recrystallization purification about "existence of compatibility." It is also possible in that case to utilize the technique of computational chemistry.

[0116] [Example 4] as an organic compound 20 which has the resin and compatibility of the resin moldings which prepares three glass tubes 10 (the outer diameter of 15mm, the bore of 12mm, die length of 200mm) which closed the end, has sublimability and is covered in each inside 20mg of crystals of cis-1, 2-dicyano -1, and 2-screw (2, 4, 5-trimethyl-3-thienyl) ethene, As a resin moldings, it is the pellet 30 (the outer diameter of about 2.5mm) of the bisphenol A polycarbonate (made in Aldrich Chemical, Inc.). die length of 2.5mm -- cylindrical -- 5-6 pieces were installed, and it exhausted until it connected the other end of a glass tube 10 to evacuation equipment 50 and the pressure in tubing was set to 10 - 5 or less Pa under the room temperature. Then, the melting sealed tube of the part near the end connection of said glass tube was carried out by the burner 60 for the glass tube sealed tubes, and said organic compound and said resin moldings were sealed in the glass sealed tube 11 which stopped both ends.

[0117] Every one of said three glass sealed tubes 11 was installed in the thermostat 70, and said glass sealed tube 11 whole was covered, and it heated in the temperature (in the case of the above-mentioned compound 110 degrees C) sublimated without said sublimability organic compound pyrolyzing, carrying out temperature control to a precision. Heating time was respectively made into 12 hours, 24 hours, and 48 hours about three. The temperature of a thermostat 70 was gradually reduced over 9 hours after heating termination to 25 degrees C. As for the crystal of said sublimability organic compound, in any case, it remained.

[0118] When optical microscope observation of a cross section was performed about said three sorts which made the heating processing time 12, 24, and 48 hours of resin pellets of each, the depth which said sublimability organic compound dissolution[ osmosis and ]-ized was 55 micrometers, 100 micrometers, and 190 micrometers from the pellet front face according to the heating processing time, respectively. That is, when a sublimability organic compound fully existed, it turned out that the thickness of the depth which said sublimability organic compound dissolution[ osmosis and ]-izes, i.e., the surface layer which carries out reforming, is controllable by the heating processing time. In addition, needless to say, the thickness of the surface layer which carries out reforming is controllable also by controlling the charge to the resin moldings of a sublimability organic compound.

[0119] [Example 5] Drawing 5 is the sectional view showing the outline configuration of resin surface layer reforming of this example, and/or coloring equipment.

[0120] As a resin moldings, coating of the dichloromethane solution of polycarbonate resin was carried out to the 1st page of the circular glass substrate 400 (for example, 0.6mm in the diameter of 120mm, thickness) with the spin coat method, and the resin film 300 (1 micrometer of thickness) which carried out degassing processing at 150 degrees C for 2 hours was used under the high vacuum of ten to 5 Pa.

[0121] On the other hand, the sublimability organic compound (for example, cis-1, 2-dicyano -1, 2-screw (2, 4, 5-trimethyl-3-thienyl) ethene) was formed with scorification on the source substrate 240 (2mm in the aluminum plate of 120mm, for example, a diameter, thickness) of sublimation, and the source of sublimation was produced.

[0122] And the above-mentioned source of sublimation was installed so that face to face might be stood against the above-mentioned resin film 300. The spacing of the resin film 300 and the formed sublimability organic compound 200 was set to 5mm. The steam of the sublimability organic compound generated from the source of sublimation arrives at a resin film front face for a short time, so that this spacing is short. However, if this spacing is shortened extremely, in case the interior of a direct-vent-system container will be made reduced pressure, an exhaust back pressure will increase. 1mm thru/or about 10mm are desirable.

[0123] The direct-vent-system container outer wall 110 consists of stainless steel or aluminum, and is made into the structure (not shown) which can be divided up and down for receipts and payments of a substrate.

[0124] It connects with the evacuation system 150 via the vacuum valve 190 and the vacuum pipe line 120, and the interior 100 of a direct-vent-system container closes a valve 190, after exhausting until the pressure inside [ 100 ] a direct-vent-system container is set to 10 - 5 or less Pa under a room temperature. Thereby, a direct-vent-system container is sealed.

[0125] What consists of aluminum which embedded the seeds electrical-and-electric-equipment exotherm of for example, a vacuum specification can be used for the heater 710 used as a heating means, the source substrate heater 720 of sublimation, the resin film glass substrate heater 740, and the vacuum valve heater 790. By installing without a clearance the heater which consists of the high quality of the material of heat-conducting characteristic, the parts of the interior 100 of a direct-vent-system container and the vacuum valve 190 can be heated to homogeneity. Here, temporarily, when the part where temperature is lower than others exists in a part of interior 100 of a direct-vent-system container, and/or vacuum valve 190, since there is a possibility that it may be cooled in the part, and the steam of the sublimability organic compound generated by sublimation may crystallize and deposit, cautions are required.

[0126] The source substrate 240 of sublimation, the source substrate heater 720 of sublimation, and the circular glass substrate 400 and the resin film glass substrate heater 740 shall be stuck by the substrate and the heater with two or more maintenance pawls (not shown), respectively.

[0127] After making reduced pressure the interior 100 of a direct-vent-system container in the case of this example, temperature control was performed to the precision so that it might heat and the whole might become the laying temperature (for example, 110 degrees C) of  $\pm 1$  degree C with the above-mentioned heating means.

[0128] Heating reduced gradually the temperature inside a stop and a direct-vent-system container over 12 hours for 24 hours to 25 degrees C. Subsequently, the interior of a direct-vent-system container was returned to atmospheric pressure, and the resin film 300 on the circular glass substrate 400 was taken out.

[0129] By measurement of the light absorption spectrum of the obtained resin film 300, optical microscope observation (usually visual field), polarization microscope observation, scanning electron microscope observation of said resin thin film front face, and transmission electron microscope observation of said resin thin film cross section, inside the resin film 300, it dissolution-ized and molecular dispersion, i.e., reforming and coloring of a surface layer are done, was checked for said sublimability organic compound. Moreover, the crystal of said sublimability organic compound was not observed the front face and inside the resin film. [ which were obtained ]

[0130] In this example, after making reduced pressure the interior 100 of a direct-vent-system container, it heated, but since heating under the vacuum using a heater advances with "radiant heat", it cannot be referred to as efficient. Especially, the large circular glass substrate 400 and the large source substrate 240 of sublimation of area are stuck at the resin film glass substrate heater 740 and the source substrate heater 720 of sublimation, respectively, and in order to improve heat transfer, it is necessary to apply thermally conductive silicone grease etc. What is necessary is just to decompress the interior 100 of a direct-vent-system container to a predetermined pressure, after heating the interior 100 of a direct-vent-system container, the direct-vent-system container outer wall 110, and the vacuum valve 190 to homogeneity to predetermined temperature under atmospheric pressure, in order to raise the effectiveness of a heating process, without using such a thing. What is necessary is just to heat it beforehand, after inert gas, such as nitrogen gas and argon gas, permutes the ambient atmosphere inside [ 100 ] a direct-vent-system container when there is a possibility that resin and a sublimability organic compound may carry out oxidation degradation by the oxygen in air, in case it heats under atmospheric pressure. If it heats in ordinary pressure, since many [ compared with the time of reduced pressure ], quantity of gas can heat efficiently the whole interior of a direct-vent-system container to homogeneity by the convection current of a gas molecule.

[0131] In addition, if the time amount taken to decompress to a predetermined pressure is long when adopting the approach of decompressing, after heating, the sublimation from a sublimability organic compound will start and a part will escape to the evacuation system 150. In order to make this loss into the minimum, it is necessary to shorten the time amount taken to decompress to a predetermined pressure as much as possible. For that purpose, what is necessary is to make small the exhaust back pressure of the vacuum valve 190 and the vacuum pipe line 120, and just to use efficient vacuum

pumps, such as a turbo molecular pump, for an evacuation system further.

[0132] If a sublimability organic compound is infiltrated into the hole of porosity particles, such as silica gel, diatomaceous earth, and a zeolite, and is beforehand used, in case the technique of performing reduced pressure after heating is used, in order to take time amount for the sublimated steam to diffuse in a direct-vent-system container from the inside of a hole, it becomes possible to reduce the loss of a reduced pressure process.

[0133] After heating, in case the technique of performing reduced pressure is used, if sublimation starts, the "heat of sublimation" according to the amount of the steam to sublimate will be taken from the source of sublimation. In order to compensate this, it is necessary to continue heating to the source of sublimation and to perform temperature control carefully. Generally, since ebullition does not advance more quickly, even if sublimation is heating in a vacuum, there are few possibilities that delay may arise in supply of the heat of sublimation.

[0134] When carrying out the high-speed exhaust air of the interior of a direct-vent-system container, it is necessary to devise so that a sublimability organic compound may not disperse. When the powder of a sublimability organic compound adheres to the front face of a resin moldings, the powder of a sublimability organic compound should permeate into the direct resin film, and there should be a possibility that the homogeneity of osmosis and distribution of the sublimability organic compound into the resin film may be spoiled.

[0135] What is necessary is just to use "the source of sublimation" which consists of one of configurations shown below, in order to carry out as [ disperse / a sublimability organic compound ].

[0136] A sublimability organic compound on the front face of the source substrate of sublimation independently (A) Coating or the formed film, (B) A sublimability organic compound and binder resin on the front face of the source substrate of sublimation Coating or formed film, (C) The porosity particle which has sunk in a sublimability organic compound on the front face of the source substrate of sublimation Coating or formed film, (D) That which sank into the front face of the source substrate of sublimation in the porosity particle and binder resin which have sunk in the sublimability organic compound, and sank into the hole of coating or the formed film, and the source substrate front face of sublimation of (E) porosity (for example, aluminum plate by which alumite processing was carried out) in the sublimability organic compound.

[0137] In case membranes are formed, when using binder resin, or there are not a sublimability organic compound and compatibility, it is desirable as a principle to choose and use what there is [ what ] no compatibility and distributes a sublimability organic compound as a crystal or a particle further. This is because "sublimation" in strict semantics will not take place temporarily if a sublimability organic compound dissolution-izes in binder resin.

[0138] In case membranes are formed, to adopt a coating method, it needs to be careful enough so that a solvent may not remain in the coating film. When a solvent is used, the residual solvent in a paint film must be removed on conditions which a sublimability organic compound does not sublimate. Since this is not an easy thing, it is desirable to adopt the coating method, for example, the coating method using ultraviolet curing mold resin or electron ray hardening mold resin, not to use a solvent, as much as possible.

[0139] When it is the compound which a sublimability organic compound tends to fuse, the approach of carrying out melting membrane formation on the source substrate of sublimation with a non-solvent is recommended.

[0140] If it is the compound which a sublimability organic compound tends to fuse, it can be made to sink in with a non-solvent into the hole of the porosity particle mentioned above or a porosity substrate. For example, scorification which is described below can be used. That is, the porosity particle of optimum dose and the impalpable powder of a sublimability organic compound are first taught to a direct-vent-system container with a vacuum valve, degassing is continued at a room temperature, and the air in the hole of a porosity particle is removed. Then, a direct-vent-system container is sealed and heated and melting of the sublimability organic compound is carried out. Subsequently, if inert gas is gradually introduced in a direct-vent-system container with a melting condition, the fused sublimability organic compound will permeate in the hole of a porosity particle. Subsequently, after cooling, the lump of the porosity particle which sinks in the sublimability

organic compound condensed with the sublimability organic compound is ground, and the sublimability organic compound sinking-in porosity particle of a desired particle size is obtained. A porosity substrate is used instead of a porosity particle, the same process is performed, and if it finally fails to write the sublimability organic compound adhering to a porosity substrate front face, a sublimability organic compound sinking-in porosity substrate can be obtained.

[0141] [Example 6] Drawing 6 is the sectional view showing the outline configuration of resin surface layer reforming of this example, and/or coloring equipment.

[0142] As an organic compound 20 which has the resin and compatibility of the resin moldings which has sublimability and is covered, cis-1, 2-dicyano -1, and 2-screw (2, 4, 5-trimethyl-3-thienyl) ethene were put into the tray 24, and it introduced into the vacuum housing C1 through the vacuum door CG 1. The interior of a vacuum housing C1 serves as the closed space C by closing the vacuum door CG 1 and the vacuum valves CB1 and JC1.

[0143] On the other hand, as a resin moldings, coating of the dichloromethane solution of polycarbonate resin was carried out to the 1st page of the circular glass substrate 400 (for example, 0.6mm in the diameter of 120mm, thickness) with the spin coat method, and the resin film 300 (1 micrometer of thickness) which carried out degassing processing at 150 degrees C for 2 hours was introduced into the vacuum housing J1 through gate valve JG1 under the high vacuum of ten to 5 Pa using the migration rail JL1. The interior of a vacuum housing J1 serves as the closed space J by closing gate valve JG1 and the vacuum valves JB1 and JC1.

[0144] The temperature in the closed space J was controlled at the same 110 degrees C as the temperature in the closed space C by controlling heating by the heater JH1 attached all over the wall of a vacuum housing J1, gate valve JG1 with a heater, and the vacuum valves JB1 and JC1 with a heater.

[0145] Moreover, the temperature in the closed space C was controlled at the same 110 degrees C as the temperature in the closed space J by controlling heating by the heater CH1 attached all over the wall of a vacuum housing C1, the heater CH2 for the vacuum doors CG 1, and the vacuum valves CB1 and JC1 with a heater. Said sublimability organic compound is sublimated as given in an example 1, without pyrolyzing in 110 degrees C.

[0146] After putting the pressure in the space C closed by opening the vacuum valve CB1 with a heater attached in the vacuum housing C1, and connecting with the evacuation system valve flow coefficient 1 on the saturation sublimation pressure condition of said sublimability organic compound, the vacuum valve CB1 was closed. In addition, if the vacuum valve CB1 is kept open, the steam of said sublimability organic compound will escape to the evacuation system valve flow coefficient 1. Then, in order to compensate the fall of whenever [ by the leak from each part of vacuum devices / reduced pressure ], it controlled so that the pressure in the space C which sometimes opened and closed the vacuum valve CB1 served as saturation sublimation pressure of said sublimability organic compound.

[0147] By, opening the vacuum valve JB1 with a heater attached in the vacuum housing J1 on the other hand, and connecting with the evacuation system JV1 After making the pressure in the closed space J below equivalent with the saturation sublimation pressure of said sublimability organic compound in said temperature (110 degrees C), in order to close the vacuum valve JB1 and to compensate the fall of whenever [ by the leak from each part of vacuum devices / reduced pressure ], It controlled so that the pressure in the space J which sometimes opened and closed the vacuum valve JB1 became the saturation sublimation pressure of said sublimability organic compound, and below equivalent.

[0148] Subsequently, opened the vacuum valve JC1 with a heater which has separated the vacuum housing C1 and the vacuum housing J1, the closed space C and the closed space J were made to connect, and it considered as the closed space M with which the closed space C and the closed space J were aligned, and temperature and a pressure were controlled so that the whole inside of closed space M will be in the saturation sublimation pressure condition of said organic compound further. Thus, it was made to be spread in the space J closed before the steam of said sublimability organic compound which it was full of in the space C closed before connection connecting. At this time, the process which the steam of said sublimability organic compound diffuses from a vacuum housing C1 to a vacuum housing J1 is promoted by opening slightly the vacuum valve JB1 from the vacuum

housing J1 to the evacuation system JV1, and controlling the pressure in a vacuum housing J1 to become lower than the inside of a vacuum housing C1. However, if the vacuum valve JB1 is kept opened wide, the steam of said sublimability organic compound will escape to the evacuation system JV1.

[0149] The interior can be made to permeate and distribute said sublimability organic compound which said resin moldings front face which placed said sublimability organic compound steam generated within the vacuum housing C1 into the vacuum housing J1 was made to adhere to homogeneity, and adhered from said resin moldings front face by controlling to said predetermined temperature and pressure as mentioned above. The vacuum valve JC1 with a heater which has separated the vacuum housing C1 and the vacuum housing J1 for this process predetermined time, for example, after making it continue for 10 minutes, is closed. Said sublimability organic compound steam which opened the vacuum valve JB1 and remained to the vacuum housing J1 interior is exhausted. After cooling the temperature of a vacuum housing J1 to near the room temperature, gate valve JG1 was opened slightly slowly, the vacuum housing J1 interior was returned to atmospheric pressure, gate valve JG1 was opened wide, and said resin moldings was taken out.

[0150] By measurement of the light absorption spectrum of the obtained resin film 300, optical microscope observation (usually visual field), polarization microscope observation, scanning electron microscope observation of said resin thin film front face, and transmission electron microscope observation of said resin thin film cross section, inside the resin film 300, it dissolution-ized and molecular dispersion, i.e., reforming and coloring of a surface layer are done, was checked for said sublimability organic compound. Moreover, the crystal of said sublimability organic compound was not observed the front face and inside the resin film. [ which were obtained ]

[0151] It becomes possible continuously about the front face of a resin moldings reforming and to color until the sublimability organic compound prepared in the vacuum housing C1 is consumed completely, keeping the temperature of a vacuum housing C1 constant by observing the above-mentioned procedure using the equipment ( drawing 6 ) of this example.

[0152] [Example 7] Drawing 7 is the sectional view showing the outline configuration of resin surface layer reforming of this example, and/or coloring equipment.

[0153] Resin surface layer reforming and/or coloring equipment of this example adjoin the vacuum housing J1 of the equipment ( drawing 6 ) of an example 6, and form a vacuum housing J2 through gate valve JG1 with a heater.

[0154] A resin moldings is put on the migration rail JL2 in a vacuum housing J2 through the vacuum door JG 2. Here, a resin moldings can be introduced in the vacuum housing J1 for resin moldings processing, without returning the pressure of the vacuum housing J1 interior for resin moldings processing to atmospheric pressure by closing the vacuum door JG 2 and gate valve JG1, opening the vacuum valve JB2, and adjusting the pressure of the vacuum housing J2 interior by the evacuation system JV2.

[0155] Furthermore, it becomes possible continuously about the front face of a resin moldings reforming and to color until the sublimability organic compound prepared in the vacuum housing C1 is consumed completely, maintaining the temperature of a vacuum housing J1 and a vacuum housing C1 without a trouble which the sublimability organic compound 20 crystalizes in the vacuum housing J2 interior by fulfilling conditions which are described below.

[0156] The temperature of a vacuum housing C1 and a vacuum housing J1 is adjusted so that the saturation sublimation pressure conditions of the sublimability organic compound 20 may be fulfilled. An example is as given in an example 6.

[0157] When opening gate valve JG1, the inside of a vacuum housing J2 is whenever [ equivalent to the vacuum housing J1 interior reduced pressure ], and the vacuum valve JC1 is closed and needs to fulfill the conditions said that the steam of a sublimability organic compound does not exist in the vacuum housing J1 interior. If this condition is not satisfied, the sublimability organic compound 20 may crystallize in the vacuum housing J2 interior.

[0158] As for the temperature of the resin moldings introduced into a vacuum housing J1, being heated to predetermined temperature before installation is desirable. This has a vacuum housing J1 in a reduced pressure condition, that of heating by radiant heat is effective, and is for a temperature up taking feelings. What is necessary is to specifically heat [ by ] to predetermined temperature under

atmospheric pressure, just before introducing into a vacuum housing J2, to decompress promptly to a vacuum housing J2, and just to transport into a vacuum housing J1 "in the state of vacuum incubation" after carrying in, to it.

[0159] After transporting the predetermined resin moldings by which time amount processing was carried out into a vacuum housing J2 within a vacuum housing J1, in order to take out in atmospheric air, it is desirable to carry out in the following procedure. First, the vacuum valve JC1 with a heater which has separated the vacuum housing C1 and the vacuum housing J1 is closed, and said sublimability organic compound steam which opened the vacuum valve JB1 and remained to the vacuum housing J1 interior is exhausted. In the meantime, the pressure of the vacuum housing J2 interior is adjusted so that it may become the J1 interior and an EQC. Subsequently, gate valve JG1 is opened, a resin moldings is transported into a vacuum housing J2 from the inside of a vacuum housing J1, and gate valve JG1 is closed. After the temperature of a resin moldings falls to predetermined temperature, the vacuum door JG 2 is opened and a resin moldings is taken out in atmospheric air. What it needs to be careful of here is the phenomenon in which said sublimability organic compound is evaporated and desorbed from a resin surface layer in the vacuum housing J2 interior of a reduced pressure condition. It cannot ignore, when it is an organic compound with high maximum vapor tension. The technique of introducing air or inert gas to the vacuum housing J2 interior for preventing this in the phase where the temperature of a resin moldings is higher than a room temperature, returning to the bottom of atmospheric pressure, and quenching a resin moldings is effective.

[0160] [Example 8] Drawing 8 is the sectional view showing the outline configuration of resin surface layer reforming of this example, and/or coloring equipment.

[0161] Resin surface layer reforming and/or coloring equipment of this example adjoin the vacuum housing J1 of the equipment ( drawing 6 ) of an example 6, form a vacuum housing J0 through gate valve JG1 with a heater, and form a vacuum housing J2 through gate valve JG2 with a heater further. Although it faces introducing a resin moldings into equipment and the same role as the vacuum housing J2 in an example 7 ( drawing 7 ) is played, the vacuum housing J0 in the equipment of this example is used only in order to transport a resin moldings to a vacuum housing J1. The vacuum housing J2 in the equipment of this example is used in order to take out a resin moldings out of equipment, or in order to send to the equipment for the following process (not shown). Or equipments for degree process, such as a sputtering system (not shown), may be formed in the vacuum-devices J2 interior.

[0162] The equipment ( drawing 7 ) indicated in the example 7 is suitable for performing only surface treatment and coloring of a resin moldings. On the other hand, the equipment of this example continues at surface treatment and coloring of a resin moldings, and is suitable for transporting a resin moldings to another processing process continuously.

[0163] A resin moldings is put on the migration rail JL0 in a vacuum housing J0 through the vacuum door JG 0. Here, a resin moldings can be introduced in the vacuum housing J1 for resin moldings processing, without returning the pressure of the vacuum housing J1 interior for resin moldings processing to atmospheric pressure by closing the vacuum door JG 0 and gate valve JG1, opening the vacuum valve JB0, and adjusting the pressure of the vacuum housing J0 interior by the evacuation system JV0.

[0164] Furthermore, it becomes possible continuously about the front face of a resin moldings reforming and to color until the sublimability organic compound prepared in the vacuum housing C1 is consumed completely, maintaining the temperature of a vacuum housing J1 and a vacuum housing C1 without a trouble which the sublimability organic compound 20 crystallizes in the vacuum housing J0 and/or vacuum housing J2 interior by fulfilling conditions which are described below.

[0165] The temperature of a vacuum housing C1 and a vacuum housing J1 is adjusted so that the saturation sublimation pressure conditions of the sublimability organic compound 20 may be fulfilled. An example is as given in an example 6.

[0166] When opening gate valve JG1, the inside of a vacuum housing J0 is whenever [ equivalent to the vacuum housing J1 interior reduced pressure ], and the vacuum valve JC1 is closed and needs to fulfill the conditions said that the steam of a sublimability organic compound does not exist in the vacuum housing J1 interior. If this condition is not satisfied, the sublimability organic compound 20



may crystallize in the vacuum housing J0 interior.

[0167] As for the temperature of the resin moldings introduced into a vacuum housing J1, being heated to predetermined temperature before installation is desirable. This has a vacuum housing J1 in a reduced pressure condition, that of heating by radiant heat is effective, and is for a temperature up taking feelings. What is necessary is to specifically heat [ by ] to predetermined temperature under atmospheric pressure, just before introducing into a vacuum housing J0, to decompress promptly to a vacuum housing J0, and just to transport into a vacuum housing J1 "in the state of vacuum incubation" after carrying in, to it.

[0168] After transporting the predetermined resin moldings by which time amount processing was carried out into a vacuum housing J2 within a vacuum housing J1, in order to take out in atmospheric air, it is desirable to carry out in the following procedure. First, the vacuum valve JC1 with a heater which has separated the vacuum housing C1 and the vacuum housing J1 is closed, and said sublimability organic compound steam which opened the vacuum valve JB1 and remained to the vacuum housing J1 interior is exhausted. In the meantime, the pressure of the vacuum housing J2 interior is adjusted so that it may become the J1 interior and an EQC. Subsequently, gate valve JG2 is opened, a resin moldings is transported into a vacuum housing J2 from the inside of a vacuum housing J1, and gate valve JG2 is closed. After the temperature of a resin moldings falls to predetermined temperature, the vacuum door JG 3 is opened, and a resin moldings is taken out in atmospheric air, or it transports to the following process. What it needs to be careful of here is the phenomenon in which said sublimability organic compound is evaporated and desorbed from a resin surface layer in the vacuum housing J2 interior of a reduced pressure condition. It cannot ignore, when it is an organic compound with high maximum vapor tension. The technique of introducing air or inert gas to the vacuum housing J2 interior for preventing this in the phase where the temperature of a resin moldings is higher than a room temperature, returning to the bottom of atmospheric pressure, and quenching a resin moldings is effective.

[0169] [Example 9] Drawing 9 is the sectional view showing the outline configuration of resin surface layer reforming of this example, and/or coloring equipment. The equipment of this example attaches the reel stands RH1 and RH2 in the vacuum housing J1 interior for resin moldings processing instead of the migration rail in the equipment ( drawing 6 ) of an example 6. By attaching the supply side reel R2 for supplying a resin film or fiber 333 to this reel stand, and the recipient reel R1 for rolling round, and rotating a recipient reel according to the device of a rotation installation machine (not shown) etc. A resin film or fiber 333 is processed continuously.

[0170] In processing, the organic compound 20 which has the resin and compatibility of the resin moldings which has sublimability and is covered is first put into a tray 24, and it introduces into a vacuum housing C1 through the vacuum door CG 1. The interior of a vacuum housing C1 serves as the closed space C by closing the vacuum door CG 1 and the vacuum valves CB1 and JC1.

[0171] On the other hand, the resin film or the fiber 333, and the recipient reel R1 which are rolled round by the supply side reel R2 are introduced into a vacuum housing J1 through gate valve JG1 as a resin moldings, it attaches in the reel stands RH2 and RH1, respectively, and a resin film or fiber 333 is rolled round from the supply side reel R2 to the recipient reel R1. The interior of a vacuum housing J1 serves as the closed space J by closing gate valve JG1 and the vacuum valves JB1 and JC1.

[0172] The temperature in the closed space J is controlled to the same temperature as the temperature in the closed space C by controlling heating by the heater JH1 attached all over the wall of a vacuum housing J1, gate valve JG1 with a heater, and the vacuum valves JB1 and JC1 with a heater. This laying temperature makes a minimum temperature sublimated without the organic compound 20 which has the resin and compatibility of the resin moldings which has sublimability and is covered pyrolyzing, and it carries out temperature control to a precision by making highest temperature into an upper limit among the temperature with which the following conditions are filled.

[0173] (a) the temperature which does not exceed the melting initiation temperature of the sublimability organic compound 20, and (b) -- the glass transition temperature of said resin, and (c) - the temperature which does not exceed the heat deformation initiation temperature of said resin, and (d) -- the temperature which does not exceed the melting initiation temperature of said resin.

[0174] Moreover, the temperature in the closed space C is controlled to the same temperature as the



temperature in the closed space J by controlling heating by the heater CH1 attached all over the wall of a vacuum housing C1, the heater CH2 for the vacuum doors CG 1, and the vacuum valves CB1 and JC1 with a heater.

[0175] After putting the pressure in the space C closed by opening the vacuum valve CB1 with a heater attached in the vacuum housing C1, and connecting with the evacuation system valve flow coefficient 1 on the saturation sublimation pressure condition of the sublimability organic compound 20, the vacuum valve CB1 is closed. In addition, if the vacuum valve CB1 is kept open, the steam of the sublimability organic compound 20 will escape to the evacuation system valve flow coefficient 1. Then, in order to compensate the fall of whenever [ by the leak from each part of vacuum devices / reduced pressure ], it controls so that the pressure in the space C which sometimes opened and closed the vacuum valve CB1 serves as saturation sublimation pressure of the sublimability organic compound 20.

[0176] By, opening the vacuum valve JB1 with a heater attached in the vacuum housing J1 on the other hand, and connecting with the evacuation system JV1 After making the pressure in the closed space J below equivalent with the saturation sublimation pressure of the sublimability organic compound 20 in said temperature, in order to close the vacuum valve JB1 and to compensate the fall of whenever [ by the leak from each part of vacuum devices / reduced pressure ], It controls so that the pressure in the space J which sometimes opened and closed the vacuum valve JB1 becomes the saturation sublimation pressure of the sublimability organic compound 20, and below equivalent.

[0177] Subsequently, open the vacuum valve JC1 with a heater which has separated the vacuum housing C1 and the vacuum housing J1, the closed space C and the closed space J are made to connect, and it considers as the closed space M with which the closed space C and the closed space J were aligned, and temperature and a pressure are controlled so that the whole inside of closed space M will be in the saturation sublimation pressure condition of said organic compound further. Thus, it is made to be spread in the space J closed before the steam of the sublimability organic compound 20 which it was full of in the space C closed before connection connecting. At this time, the process which the steam of the sublimability organic compound 20 diffuses from a vacuum housing C1 to a vacuum housing J1 is promoted by opening slightly the vacuum valve JB1 from the vacuum housing J1 to the evacuation system JV1, and controlling the pressure in a vacuum housing J1 to become lower than the inside of a vacuum housing C1. However, if the vacuum valve JB1 is kept opened wide, the steam of the sublimability organic compound 20 will escape to the evacuation system JV1. [0178] Into the vacuum housing J1 with which the steam of the sublimability organic compound 20 was filled, a recipient reel is rotated and a resin film or fiber 333 is moved from a supply side reel to a recipient reel by part for constant speed, for example, 10mm./.

[0179] The interior can be made to permeate and distribute the sublimability organic compound 20 which the front face of the resin film which placed sublimability organic compound 20 steam generated within the vacuum housing C1 as mentioned above into the vacuum housing J1, or fiber 333 was made to adhere to homogeneity, and adhered from said resin moldings front face.

[0180] After all of the resin film prepared by the supply side reel R2 or fiber 333 reach the recipient reel R1, The vacuum valve JC1 with a heater which has separated the vacuum housing C1 and the vacuum housing J1 is closed. Sublimability organic compound 20 steam which opened the vacuum valve JB1 and remained to the vacuum housing J1 interior is exhausted. After cooling the temperature of a vacuum housing J1 to near the room temperature, gate valve JG1 is opened slightly slowly, the vacuum housing J1 interior is returned to atmospheric pressure, and the resin film or fiber 333 which opened gate valve JG1 wide and was rolled round by the reel R1 is taken out.

[0181] The equipment of this example can make a photochromic function able to give the surface layer of fiber, or is the purpose to which an ultraviolet absorption function is made to give, and can be especially used for a sheet-plastic surface layer suitably. Furthermore, it can use also for the purpose which gives a pharmacological activity function and the function as agricultural chemicals to a sheet-plastic surface layer.

[0182] [Example 10] A plastic optical fiber is used instead of the resin film in an example 9, or fiber 333, and also the surface layer of a plastic optical fiber is reformed like an example 9, the refractive index of a surface layer can be changed or a photochromic function and a fluorescence function can be given.

[0183] [Example 11] Change at cis-1, the 2-dicyano -1, and 2-screw (2, 4, 5-trimethyl-3-thienyl) ethene which were used as an organic compound which has the resin and compatibility of the resin moldings which has sublimability and is covered in an example 1, and 9 and 10-diphenyl anthracene are used. It changes to the pellet of the bisphenol A polycarbonate used as a resin moldings in the example 1. The pellet of the poly ape phone (made in Aldrich Chemical, Inc.) (the outer diameter of about 2.5mm) die length of 3mm -- being cylindrical -- used, changed to 110 degrees C whenever [ in an example 1 / stoving temperature ], made processing temperature into 150 degrees C, changed in processing-time 24 hours in an example 1, and the processing time was made into 48 hours, and also it processed like the example 1.

[0184] When this pellet was put on the dark place and the ultraviolet ray lamp was irradiated, skillful blue fluorescence was observed from the pellet front face. That is, said sublimability organic compound permeates and distributes, reforming of the surface layer is carried out to the surface layer of polycarbonate resin, and it turns out that the function which presents fluorescence was given.

[0185] [Example 12] Drawing 12 is the sectional view showing the outline configuration of resin surface layer reforming of this example, and/or coloring equipment. This equipment is suitable for surface layer reforming of powdered resin, and/or coloring.

[0186] As an organic compound 20 which has the resin and compatibility of the resin moldings which has sublimability and is covered, cis-1, 2-dicyano -1, and 2-screw (2, 4, 5-trimethyl-3-thienyl) ethene were put into the tray 24, and it introduced into the vacuum housing C1 through the vacuum door CG 1. The interior of a vacuum housing C1 serves as the closed space C by closing the vacuum door CG 1 and the vacuum valves CB1 and JC1.

[0187] On the other hand, the non-colored type (mean particle diameter of 20 micrometers) of thermosetting acrylic modified resin impalpable powder "a RABUKO roll" (Dainichiseika Colour & Chemicals Mfg. Co., Ltd. make) was introduced into the vacuum housing J1 through the vacuum door JG 4 with churning equipment as a resin moldings. The vacuum valves JC1 and JB1 shall be completely closed at the time of installation. In addition, the interior of a vacuum housing J1 serves as the closed space J by closing the vacuum door JG 4 and the vacuum valves JB1 and JC1.

[0188] The temperature in the closed space J was controlled at the same 110 degrees C as the temperature in the closed space C by controlling heating by the vacuum valves JB1 and JC1 with the heater JH1 attached all over the wall of a vacuum housing J1, the heater for the vacuum doors JG 4, and a heater under atmospheric pressure (i.e., the condition of having opened the vacuum door JG 4 slightly). Furthermore, using the impeller driven by the magnet coupling type churning motor attached by the vacuum door JG 4, the powdered resin in a vacuum housing J1 was stirred so that all powdered resin might become the above-mentioned temperature. After the temperature of powdered resin reached the above-mentioned temperature, the vacuum door JG 4 was closed completely.

[0189] Moreover, the temperature in the closed space C was controlled at the same 110 degrees C as the temperature in the closed space J by controlling heating by the heater CH1 attached all over the wall of a vacuum housing C1, the heater CH2 for the vacuum doors CG 1, and the vacuum valves CB1 and JC1 with a heater. Said sublimability organic compound is sublimated as given in an example 1, without pyrolyzing in 110 degrees C.

[0190] After putting the pressure in the space C closed by opening the vacuum valve CB1 with a heater attached in the vacuum housing C1, and connecting with the evacuation system valve flow coefficient 1 on the saturation sublimation pressure condition of said sublimability organic compound, the vacuum valve CB1 was closed. In addition, if the vacuum valve CB1 is kept open, the steam of said sublimability organic compound will escape to the evacuation system valve flow coefficient 1. Then, in order to compensate the fall of whenever [ by the leak from each part of vacuum devices / reduced pressure ], it controlled so that the pressure in the space C which sometimes opened and closed the vacuum valve CB1 served as saturation sublimation pressure of said sublimability organic compound.

[0191] On the other hand, the pressure in the closed space J was made below equivalent with the saturation sublimation pressure of said sublimability organic compound in said temperature (110 degrees C) by opening the vacuum valve JB1 with a heater attached in the vacuum housing J1 little by little, and connecting with the evacuation system JV1, stirring the powdered resin in a vacuum housing J1 using the impeller driven by the magnet coupling type churning motor attached by the

vacuum door JG 4. Under the present circumstances, if the vacuum valve JB1 is opened rapidly, since powdered resin will soar violently, cautions are required. Subsequently, in order to close the vacuum valve JB1 and to compensate the fall of whenever [ by the leak from each part of vacuum devices / reduced pressure ], it controlled so that the vacuum valve JB1 was sometimes opened and the pressure in the closed space J became the saturation sublimation pressure of said sublimability organic compound, and below equivalent.

[0192] Next, opened the vacuum valve JC1 with a heater which has separated the vacuum housing C1 and the vacuum housing J1, the closed space C and the closed space J were made to connect, and it considered as the closed space M with which the closed space C and the closed space J were aligned, and temperature and a pressure were controlled so that the whole inside of closed space M will be in the saturation sublimation pressure condition of said organic compound further. Moreover, stirring the powdered resin in a vacuum housing J1 was continued using the impeller driven by the magnet coupling type churning motor attached by the vacuum door JG 4. Thus, it was made to be spread in the space J closed before the steam of said sublimability organic compound which it was full of in the space C closed before connection connecting. At this time, the process which the steam of said sublimability organic compound diffuses from a vacuum housing C1 to a vacuum housing J1 is promoted by opening slightly the vacuum valve JB1 from the vacuum housing J1 to the evacuation system JV1, and controlling the pressure in a vacuum housing J1 to become lower than the inside of a vacuum housing C1. However, if the vacuum valve JB1 is kept opened wide, the steam of said sublimability organic compound will escape to the evacuation system JV1.

[0193] The interior can be made to permeate and distribute said sublimability organic compound which said sublimability organic compound steam generated within the vacuum housing C1 was made to adhere to homogeneity on the front face of the powdered resin stirred within the vacuum housing J1, and adhered from said resin moldings front face by controlling to said predetermined temperature and pressure as mentioned above. The vacuum valve JC1 with a heater which has separated the vacuum housing C1 and the vacuum housing J1 for this process predetermined time, for example, after making it continue for 12 hours, is closed. Said sublimability organic compound steam which opened the vacuum valve JB1 and remained to the vacuum housing J1 interior is exhausted. After cooling the temperature of a vacuum housing J1 to near the room temperature, the vacuum door JG 4 was opened slightly slowly, the vacuum housing J1 interior was returned to atmospheric pressure, the vacuum door JG 4 was opened wide completely, and said resin moldings was taken out.

[0194] By the optical microscope of powdered resin and scanning microscope observation which were obtained, it was checked that the whole front face of powdered resin is colored homogeneity with said photochromic compound. Moreover, existence of the microcrystal of a photochromic compound was not checked in powdered resin.

[0195] The obtained powdered resin changes with the exposures of ultraviolet rays to yellow at red by the exposure of the visible ray and/or infrared radiation which omitted ultraviolet rays. That is, functioning as powdered photochromic resin was checked by having carried out reforming of the surface layer of powdered resin.

[0196] [Example 13] It changed to the polycarbonate resin thin film formed in the 1st page of the circular glass substrate 400 in an example 6 as a resin moldings, and the stand holding the edge of said plastic lens was used using the Pori (methyl methacrylate) plastic lens, and also the surface layer of a plastic lens was reformed like the example 6 using said photochromic coloring matter, and the follow clo MIKKU function was given.

[0197] Even if it uses that to which resin coating of the front face of a glass lens was carried out instead of said plastic lens, similarly, a surface layer can be reformed using said photochromic coloring matter, and a follow clo MIKKU function can be given.

[0198] Moreover, as an organic compound which has the resin and compatibility of the resin moldings which has sublimability and is covered, instead of said photochromic coloring matter, the surface layer of a plastic lens or a resin coat lens can be reformed, and it can also be colored the color of arbitration by using usual sublimability coloring matter.

[0199] [an example 14] -- as a resin moldings in a screw vial with a capacity of 50ml with 5-6 pellets (the outer diameter of about 2.5mm, and die length of 2.5mm -- cylindrical) of the bisphenol A

polycarbonate (made in Aldrich Chemical, Inc.) The crystal of a ferrocene carboxy aldehyde (made in Aldrich Chemical, Inc.; melting point of 117 degrees C) is installed as an organic compound 20 which has the resin and compatibility of the resin moldings which has sublimability and is covered. The lid of a screw vial was sealed, said screw vial was put into 120 degrees C to the thermostat which carried out a temperature setup, and it heated under atmospheric pressure. Sublimation of a ferrocene carboxy aldehyde starts in connection with the temperature rise inside a screw vial, and the interior reaches a maximum-vapor-tension condition. After continuing heating for 4 hours, to the room temperature, 4 hours was required and it cooled.

[0200] The surface layer of the obtained polycarbonate pellet was colored vivid orange peculiar to a ferrocene derivative.

[0201] When the cross section of the obtained polycarbonate pellet was observed and analyzed by the X-ray microanalyser attached in the scanning electron microscope, it was checked that the iron element is distributed from the front face of a pellet covering a depth of about 10 micrometers. That is, inside said resin pellet, it dissolution-ized and molecular dispersion, i.e., reforming and coloring of a surface layer are done, was checked for said sublimability organic compound.

[0202] [Example 15] 20g (mp178 degree C; Wako Pure Chem make) of camphor put into ten commercial hangers for the clothes made from polypropylene and a commercial glass evaporating dish as a resin moldings is put in into a vacuum dryer (DP41 mold made from the Yamato science). Seal a vacuum door and close the vacuum valve of an inlet completely, and heating is begun where the vacuum valve of an exhaust port is opened slightly. When internal wall surface temperature reached 100 degrees C, the vacuum valve of an exhaust port was closed completely and it considered as the sealing condition, and heating was continued, controlling temperature so that internal temperature becomes 100 degrees C thru/or 105 degrees C. Internal temperature was maintained at said temperature requirement for 2 hours, after observing the camphor in a glass evaporating dish and sublimating completely from the observation port of a vacuum dryer. Subsequently, after it opened the inlet for heating after cooling radiationally for 12 hours, a stop and, and making internal pressure into atmospheric pressure, the vacuum door was opened and the hanger was taken out. The crystal of camphor did not deposit on the interior of a vacuum dryer, and the front face of a hanger. When it measured one weight of a hanger at a time, an average of 2g and weight were increasing. It is judged as what camphor permeated and distributed and weight increased to the surface layer of a hanger. Thus, the hanger for the clothes made from polypropylene by which reforming of the surface layer was carried out demonstrates the insect control function which camphor has for a long period of time.

[0203] [Example 3 of a comparison] Although camphor was kneaded and injection molding was tried in polypropylene, loss in quantity by sublimation of camphor was remarkable, and it was difficult to obtain the moldings whose presentation was fixed. Moreover, since a lot of camphor steams occurred in work environment, in order to be work environment and atmospheric-air maintenance, it turned out that a local exhaust ventilation and an exhaust air processor are newly needed.

[0204] Next, the approach of dipping the hanger for the clothes made from polypropylene in the toluene solution of camphor, and infiltrating camphor into a surface layer was tried. Although it was checked that a certain amount of quantity of camphor sinks in, since the toluene used as a solvent also permeates into polypropylene, if it remains as it is, it cannot be used as an object for daily necessities. Then, when long duration heating reduced pressure drying was performed at 60 degrees C among the vacuum dryer and toluene was removed completely, the camphor weight in a hanger was about [ in the case of an example 15 ] 1/50. Compared with the approach of an example 15, it turned out that effectiveness is remarkably bad.

[0205]

[Effect of the Invention] As mentioned above, the resin moldings with which reforming of the equipment and the surface layer the reforming approach of the resin moldings surface layer of this invention and for it was carried out as explained to the detail, And according to the resin moldings with which the equipment and the surface layer the coloring approach of a resin moldings surface layer and for it were colored, and the resin moldings to which functionality was given by reforming of a surface layer It consists of a sublimability organic compound and resin, and the surface layer

with these uniform presentations by which reforming was carried out is produced on the front face of a resin moldings, The surface layer which contains a sublimability organic compound and does not contain an volatile impurity and by which reforming was carried out is produced on the front face of a resin moldings, It consists of a sublimability organic compound and resin, and the surface layer with these uniform presentations by which reforming was carried out is efficiently produced on the front face of a resin moldings, The surface layer containing a sublimability organic compound by which reforming was carried out is produced on the front face of a resin moldings, without spoiling the surface smooth nature of a resin moldings, When micro processing is performed to the front face of a resin moldings, produce the surface layer containing a sublimability organic compound by which reforming was carried out on the front face of a resin moldings, without spoiling this surface structure, The surface layer containing the sublimability organic compound of an extensive class by which reforming was carried out is produced on the front face of a resin moldings, The surface layer which contained thickness and/or a sublimability organic compound with a uniform presentation without complicated mechanical control and by which reforming was carried out is produced on the front face of a resin moldings, It becomes possible to produce the surface layer which was not concerned with the size of the area of a surface layer, but contained the sublimability organic compound which has uniform thickness and/or a uniform presentation and by which reforming was carried out on the front face of a resin moldings, and to offer a resin moldings with the surface layer which has the above-mentioned description and by which reforming was carried out.

[0206] Furthermore, the thing for which it consists of sublimability coloring matter and resin, and the colored surface layer with these uniform presentations is produced on the front face of a resin moldings, The colored surface layer which contains sublimability coloring matter and does not contain an volatile impurity is produced on the front face of a resin moldings, It consists of sublimability coloring matter and resin, and the colored surface layer with these uniform presentations is efficiently produced on the front face of a resin moldings, The colored surface layer containing sublimability coloring matter is produced on the front face of a resin moldings, without spoiling the surface smooth nature of a resin moldings, When micro processing is performed to the front face of a resin moldings, produce the colored surface layer containing sublimability coloring matter on the front face of a resin moldings, without spoiling this surface structure, The colored surface layer containing the sublimability coloring matter of an extensive class is produced on the front face of a resin moldings, The colored surface layer which contained thickness and/or sublimability coloring matter with a uniform presentation without complicated mechanical control is produced on the front face of a resin moldings, The colored surface layer which was not concerned with the size of the area of a surface layer, but contained the sublimability coloring matter which has uniform thickness and/or a uniform presentation is produced on the front face of a resin moldings, Above The resin moldings with which functionality was given to the surface layer can be offered by having carried out reforming of a resin moldings with the colored surface layer which has the description, and the surface layer.

[0207] Moreover, functionality can be given to the surface layer of a resin moldings by the amount of the high-performance material used far fewer than the case where knead high-performance material to the whole resin, and functionality is given to it.

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[Translation done.]

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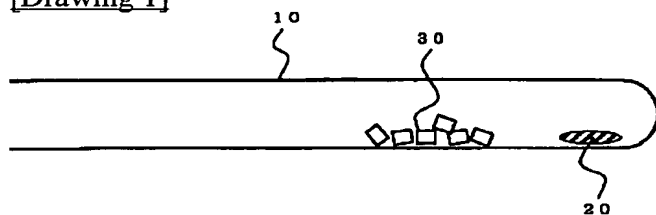
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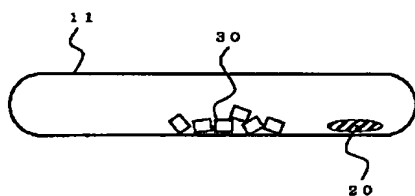
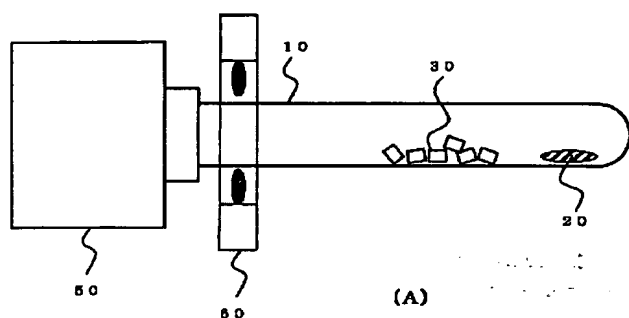
DRAWINGS

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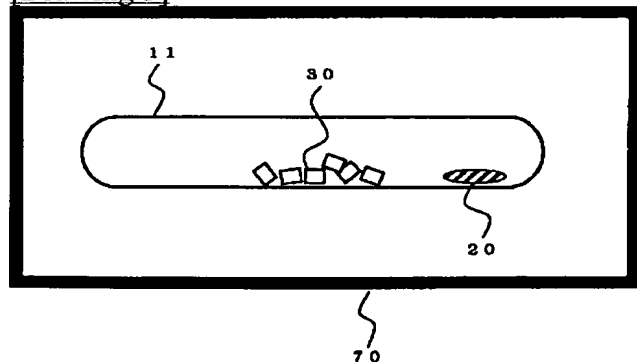
[Drawing 1]



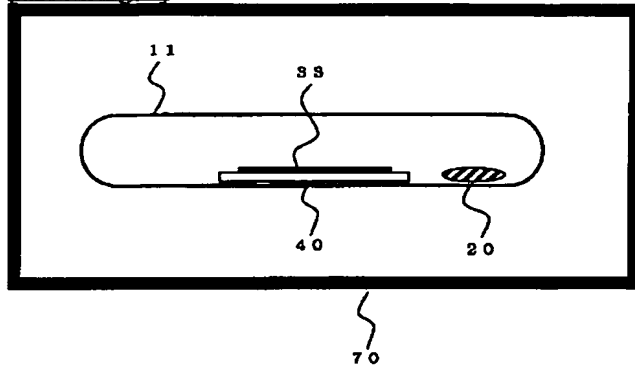
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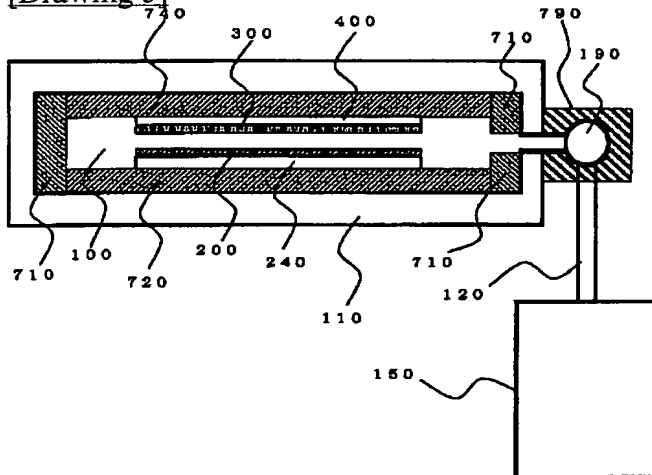
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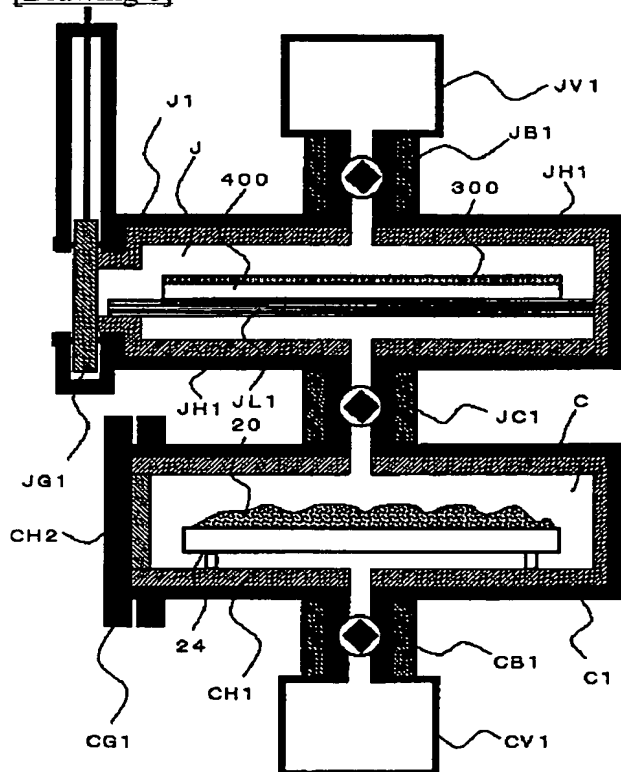
[Drawing 4]



[Drawing 5]

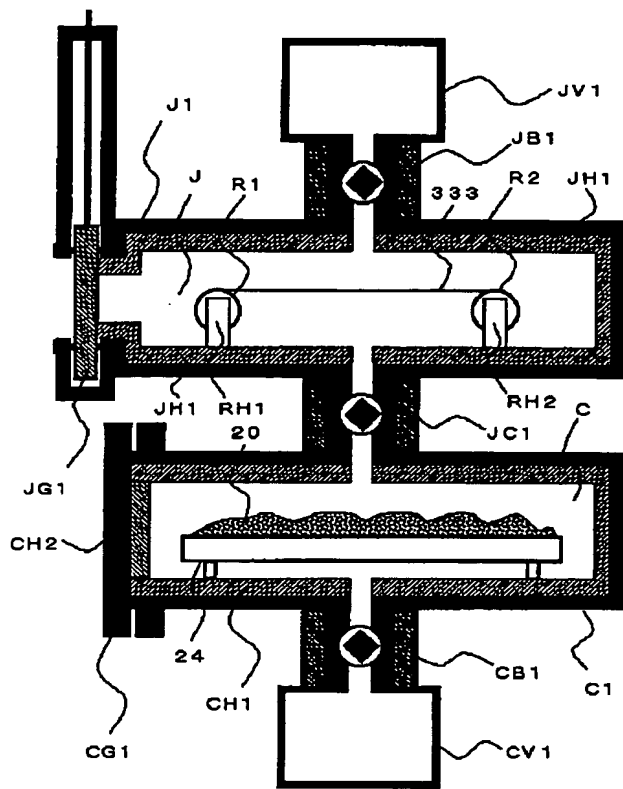


[Drawing 6]

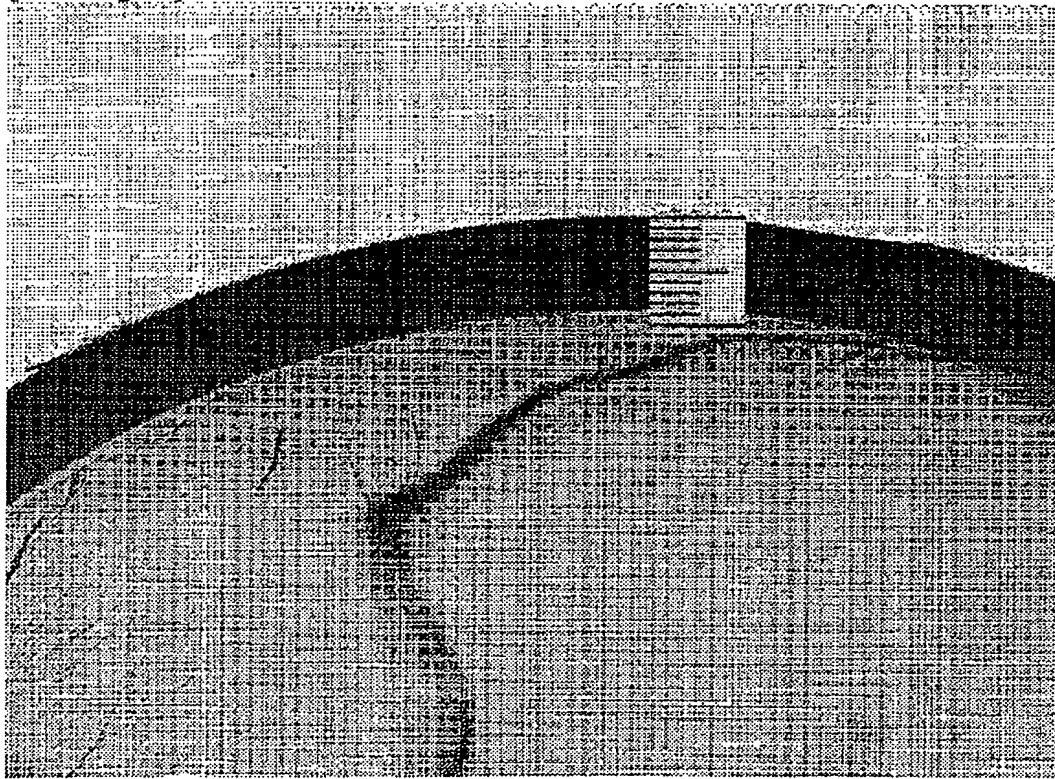




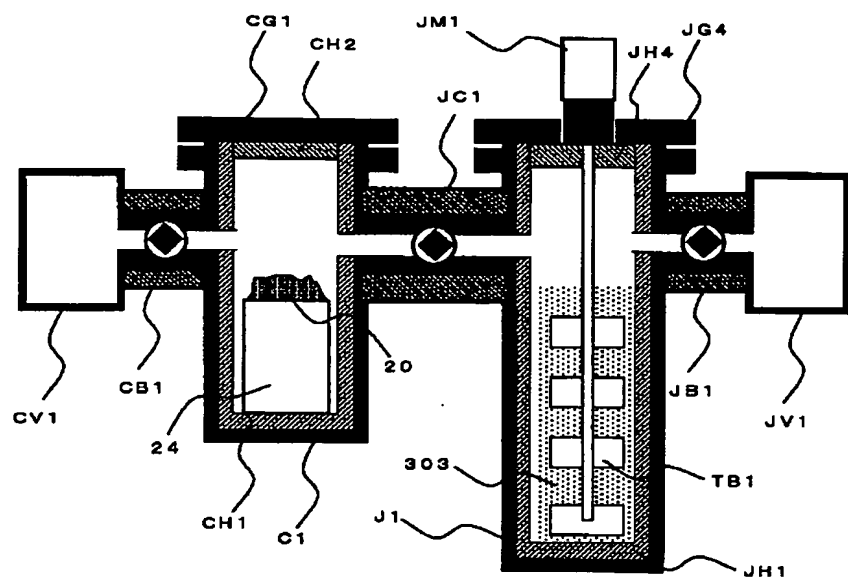




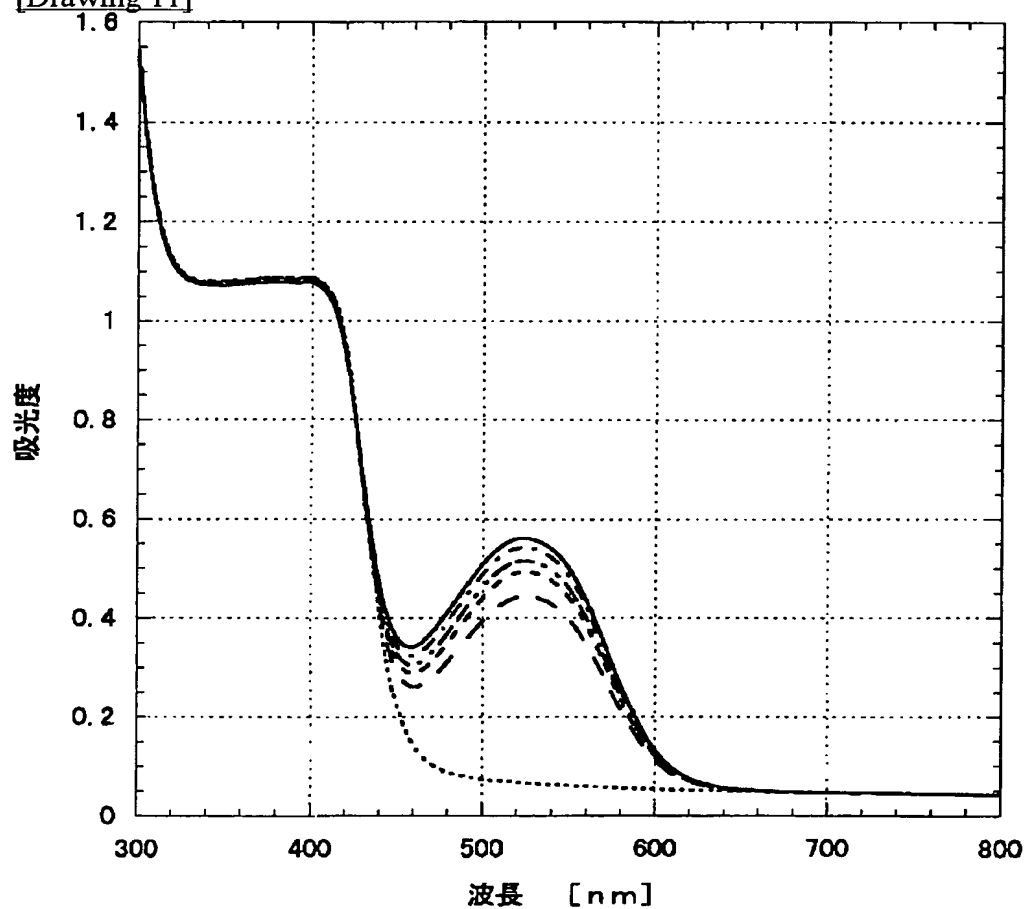
[Drawing 10]



[Drawing 12]



[Drawing 11]



[Translation done.]

**MODIFICATION OF SURFACE LAYER OF RESIN MOLDED MATERIAL, DEVICE THEREFOR AND RESIN MOLDED MATERIAL OF WHICH SURFACE LAYER IS MODIFIED, AND COLORING OF SURFACE LAYER OF RESIN MOLDED MATERIAL, DEVICE THEREFOR AND RESIN MOLDED MATERIAL OF WHICH SURFACE LAYER IS COLORED, AND RESIN FORMED MATERIAL IMPARTED WITH FUNCTIONALITY BY SURFACE MODIFICATION**

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**Classification:**  
**- international:** C08J7/00; C08J7/06; C08J7/00; (IPC1-7): C08J7/06; A61K9/70; B29C71/00; D06M23/00; G02B1/10; G02B6/00  
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**Application number:** JP19990091038 19990331  
**Priority number(s):** JP19990091038 19990331

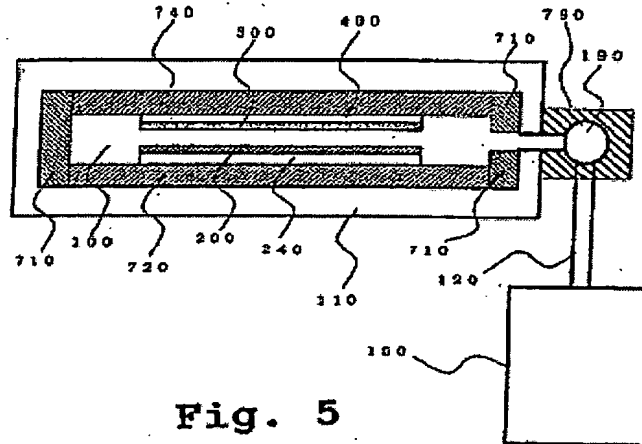
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**Abstract of JP2000281821**

**PROBLEM TO BE SOLVED:** To perform a modification and/or coloring of a resin surface layer by penetrating/dispersing an organic compound having an affinity to the resin and a sublimating property on the surface of the resin formed material. **SOLUTION:** This method for modifying and coloring a surface of a resin is provide by putting a resin formed material and an organic compound having an affinity to the resin and also a sublimating property in a hermetically closed container, and adjusting inside pressure and temperature to make a saturated sublimation pressure state for uniformly attaching the organic compound on the surface of the resin formed material and further penetrating/dispersing to its inside. Also, by modifying the surface of the resin, it is possible to impart functionality to it.



**Fig. 5**

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最終頁に続く

(54) 【発明の名称】 樹脂成形物表面層の改質方法およびそのための装置および表面層が改質された樹脂成形物、および樹脂成形物表面層の着色方法およびそのための装置および表面層が着色された樹脂成形物、お

(57) 【要約】

【課題】 樹脂成形物の表面へ前記樹脂と親和性があり、かつ昇華性の有機化合物を均一に浸透・分散させ、樹脂表面層の改質および／または着色を行う。

【解決手段】 樹脂成形物、および、前記樹脂と親和性があり、かつ昇華性の有機化合物とを密閉式容器に入れ、内部の圧力および温度を調節して前記有機化合物の飽和昇華圧状態に置くことによって、前記有機化合物蒸気が前記樹脂成形物表面に均一に付着し、更に、内部に浸透・分散していくようにし、樹脂表面層の改質および／または着色を行うことができる。また、樹脂表面層の改質により機能性を付与することができる

**【特許請求の範囲】**

【請求項1】 昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する有機化合物と、前記樹脂成形物とを、閉じた空間内に載置し、前記閉じた空間内を前記有機化合物の飽和昇華圧状態に置き、前記有機化合物蒸気を前記樹脂成形物表面に均一に付着させ、付着した前記有機化合物を前記樹脂成形物表面から内部に浸透・分散させることを特徴とする樹脂成形物表面層の改質方法。

【請求項2】 昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する有機化合物を閉じた空間C内に載置し、一方、前記樹脂成形物を閉じた空間J内に載置し、閉じた空間J内の温度を、閉じた空間C内の温度と同一または閉じた空間C内の温度よりも高く制御し、閉じた空間C内の圧力を前記有機化合物の飽和昇華圧状態に置き、閉じた空間J内の圧力を、閉じた空間C内の圧力と同一または閉じた空間C内の圧力よりも低く制御し、次いで、閉じた空間Cと閉じた空間Jとを連結させて、閉じた空間Cと閉じた空間Jとを合わせた閉じた空間Mとし、更に、閉じた空間M内全体が前記有機化合物の飽和昇華圧状態になるよう温度および圧力を制御し、連結前の閉じた空間C内に充満した前記有機化合物の蒸気が連結前の閉じた空間J内に拡散するようにし、前記有機化合物蒸気を前記樹脂成形物表面に均一に付着させ、付着した前記有機化合物を前記樹脂成形物表面から内部に浸透・分散させることを特徴とする樹脂成形物表面層の改質方法。

【請求項3】 請求項1に記載の樹脂成形物表面層の改質方法において、前記有機化合物は、前記樹脂成形物表面に付着可能なように、以下の(A)～(E)の5つの態様からなる群の中から選択される少なくとも1つの態様で、昇華源基板に付着または含有されていることを特徴とする樹脂表面層の改質方法。

(A) 前記有機化合物が単独で昇華源基板の表面に塗工または成膜されている、

(B) 前記有機化合物とバインダー樹脂とが昇華源基板の表面に塗工または成膜されている、

(C) 前記有機化合物を含浸している多孔質粒子が昇華源基板の表面に塗工または成膜されている、

(D) 前記有機化合物を含浸している多孔質粒子とバインダー樹脂とが昇華源基板の表面に塗工または成膜されている、

(E) 多孔性の昇華源基板表面の孔に前記有機化合物が含浸されたもの。

【請求項4】 請求項3に記載の樹脂表面層の改質方法において、

上記(A)～(E)のいずれかの態様でその表面に前記有機化合物を付着または含有する前記昇華源基板の表面を前記樹脂成形物表面の近傍に配置することを特徴とする樹脂表面層の改質方法。

【請求項5】 請求項1に記載の樹脂表面層の改質方法において、

前記樹脂成形物および前記有機化合物を真空容器に入れ、前記真空容器に設けられた真空弁から排気して前記真空容器内の圧力を、室温以上であって前記有機化合物および／または前記樹脂の熱分解温度を越えない温度における前記有機化合物の飽和昇華圧まで減圧し、前記真空容器に設けられた真空弁をすべて密閉して閉じた空間とし、密閉された前記真空容器内部の温度を、上記減圧状態において前記有機化合物の分圧が飽和昇華圧に到達する温度まで加熱し、所定時間加熱後、前記真空容器を徐冷することを特徴とする樹脂表面層の改質方法。

【請求項6】 請求項3に記載の樹脂表面層の改質方法において前記請求項3に記載のいずれかの態様で昇華源基板に付着または含有された前記有機化合物および前記樹脂成形物を、真空容器に入れ、前記真空容器に設けられた真空弁から排気して前記真空容器内の圧力を、室温以上であって前記有機化合物および／または前記樹脂の熱分解温度を越えない温度における前記有機化合物の飽和昇華圧まで減圧し、前記真空容器に設けられた真空弁をすべて密閉して閉じた空間とし、密閉された前記真空容器内部の温度を、上記減圧状態において前記有機化合物の分圧が飽和昇華圧に到達する温度まで加熱し、所定時間加熱後、前記真空容器を徐冷することを特徴とする樹脂表面層の改質方法。

【請求項7】 請求項4に記載の樹脂表面層の改質方法において、

前記請求項3に記載のいずれかの態様で昇華源基板に付着または含有された前記有機化合物および前記樹脂成形物を、真空容器に入れ、前記真空容器に設けられた真空弁から排気して前記真空容器内の圧力を、室温以上であって前記有機化合物および／または前記樹脂の熱分解温度を越えない温度における前記有機化合物の飽和昇華圧まで減圧し、前記真空容器に設けられた真空弁をすべて密閉して閉じた空間とし、密閉された前記真空容器内部の温度を、上記減圧状態において前記有機化合物の分圧が飽和昇華圧に到達する温度まで加熱し、

所定時間加熱後、徐冷することを特徴とする樹脂表面層の改質方法。

【請求項 8】 請求項 1 に記載の樹脂表面層の改質方法において、

前記樹脂成形物および前記有機化合物を真空容器に入れ、

前記真空容器内部の温度を室温以上であって、前記有機化合物および／または前記樹脂の熱分解温度を越えない温度まで加熱し、

上記温度に保ちながら、前記真空容器に設けられた真空弁から排気して前記真空容器内の圧力を、上記温度における前記有機化合物の飽和昇華圧まで減圧し、

前記真空容器に設けられた真空弁をすべて密閉して閉じた空間とし、

所定時間加熱減圧後、前記真空容器を徐冷することを特徴とする樹脂表面層の改質方法。

【請求項 9】 請求項 3 に記載の樹脂表面層の改質方法において、

前記請求項 3 に記載のいずれかの態様で昇華源基板に付着または含有された前記有機化合物および前記樹脂成形物を、真空容器に入れ、

前記真空容器内部の温度を室温以上であって、前記有機化合物および／または前記樹脂の熱分解温度を越えない温度まで加熱し、

上記温度に保ちながら、前記真空容器に設けられた真空弁から排気して前記真空容器内の圧力を、上記温度における前記有機化合物の飽和昇華圧まで減圧し、

前記真空容器に設けられた真空弁をすべて密閉して閉じた空間とし、

所定時間加熱減圧後、前記真空容器を徐冷することを特徴とする樹脂表面層の改質方法。

【請求項 10】 請求項 4 に記載の樹脂表面層の改質方法において、

前記請求項 3 に記載のいずれかの態様で昇華源基板に付着または含有された前記有機化合物および前記樹脂成形物を、真空容器に入れ、

前記真空容器内部の温度を室温以上であって、前記有機化合物および／または前記樹脂の熱分解温度を越えない温度まで加熱し、

上記温度に保ちながら、前記真空容器に設けられた真空弁から排気して前記真空容器内の圧力を、上記温度における前記有機化合物の飽和昇華圧まで減圧し、

前記真空容器に設けられた真空弁をすべて密閉して閉じた空間とし、

所定時間加熱減圧後、前記真空容器を徐冷することを特徴とする樹脂表面層の改質方法。

【請求項 11】 請求項 2 に記載の樹脂表面層の改質方法において、

昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する有機化合物を、排気系への配管および前記有機

化合物導入部および真空容器 J 1 への接続配管を設けた真空容器 C 1 に入れ、前記有機化合物導入部および真空容器 J 1 への接続配管を閉じてから前記排気系より真空容器 C 1 内の圧力を、室温以上であって前記有機化合物および／または前記樹脂の熱分解温度を越えない温度における前記有機化合物の飽和昇華圧まで減圧し、真空容器 C 1 内の温度を前記温度まで加熱し、

一方、前記樹脂成形物を、排気系への配管および前記樹脂成形物導入部および真空容器 C 1 への接続配管を設けた真空容器 J 1 に入れ、前記樹脂成形物導入部および真空容器 C 1 への接続配管を閉じ、

真空容器 J 1 内の温度を、真空容器 C 1 内の温度と同一または真空容器 C 1 内の温度よりも高く制御し、

真空容器 C 1 内の圧力を前記有機化合物の飽和昇華圧状態に置き、

真空容器 J 1 内の圧力を、真空容器 C 1 内の圧力と同一または真空容器 C 1 内の圧力よりも低く制御し、

次いで、真空容器 C 1 と真空容器 J 1 とを相互の接続配管を通じて連結させて、真空容器 C 1 内の閉じた空間 C と真空容器 J 1 内の閉じた空間 J とを合わせた閉じた空間 M とし、更に、閉じた空間 M 内全体が前記有機化合物の飽和昇華圧状態になるよう温度および圧力を制御し、連結前の真空容器 C 1 内に充満した前記有機化合物の蒸気が連結前の真空容器 J 1 内に拡散するようにし、前記有機化合物蒸気を前記樹脂成形物表面に均一に付着させ、

付着した前記有機化合物を前記樹脂成形物表面から内部に浸透・分散させるため所定時間加熱した後、

真空容器 C 1 と真空容器 J 1 とを相互に連結している接続配管を閉じ、

真空容器 J 1 内部に残留している前記有機化合物の蒸気が前記樹脂成形物表面から内部に浸透・分散するよう真空容器 J 1 内の温度および圧力を所定時間制御し、

真空容器 J 1 内部に前記有機化合物の蒸気が過剰に存在している場合は排気系から真空容器 J 1 外部へ排出し、

次いで、真空容器 J 1 内の前記樹脂成形物の温度を常温へ戻すことを特徴とする樹脂表面層の改質方法。

【請求項 12】 請求項 11 に記載の樹脂表面層の改質方法において、

最終段階で真空容器 J 1 内の前記樹脂成形物の温度を常温へ戻す替わりに、

ゲート弁を通じて真空容器 J 1 に隣接して設けられ、独立して圧力制御可能な真空容器 J 2 内へ、前記樹脂成形物を減圧下で移送してから前記樹脂成形物の温度を常温へ戻すことを特徴とする樹脂表面層の改質方法。

【請求項 13】 請求項 5、請求項 6、請求項 7、請求項 8、請求項 9、請求項 10、請求項 11、または、請求項 12 に記載の樹脂表面層の改質方法において、

前記有機化合物蒸気を前記樹脂成形物表面に均一に付着させ、

付着した前記有機化合物を前記樹脂成形物表面から内部に浸透・分散させるために、前記樹脂成形物の温度を前記樹脂のガラス転移温度以上であって、前記有機化合物および／または前記樹脂の熱分解温度を越えない温度まで加熱することを特徴とする樹脂表面層の改質方法。

【請求項 14】 請求項 1、請求項 2、請求項 3、請求項 4、請求項 5、請求項 6、請求項 7、請求項 8、請求項 9、請求項 10、請求項 11、または、請求項 12 に記載の樹脂表面層の改質方法において、前記有機化合物として、昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する色素を用いることによって前記樹脂成形物の表面層を改質すると同時に着色することを特徴とする樹脂表面層の着色方法。

【請求項 15】 請求項 13 に記載の樹脂表面層の改質方法において、前記有機化合物として、昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する色素を用いることによって前記樹脂成形物の表面層を改質すると同時に着色することを特徴とする樹脂表面層の着色方法。

【請求項 16】 昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する有機化合物、および、前記樹脂成形物を、前記有機化合物の飽和昇華圧状態に置くための密閉可能な容器と、前記密閉可能な容器の圧力を調整するための排気系と、前記有機化合物が昇華して有機化合物の蒸気が前記樹脂成形物表面に付着した後、更に前記有機化合物が前記樹脂成形物中に浸透・分散するための加熱手段と、を設けたことを特徴とする樹脂表面層の改質装置。

【請求項 17】 請求項 16 に記載の樹脂成形物表面層の改質装置であって、更に、前記有機化合物が、前記樹脂成形物表面に付着可能なように、上記 5 つの態様からなる群の中から選択される少なくとも 1 つの態様で、保持されるための昇華源基板を設けたことを特徴とする樹脂表面層の改質装置。

【請求項 18】 昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する有機化合物を、飽和昇華圧状態に置くための密閉可能な真空容器 C 1 と、前記樹脂成形物を、前記有機化合物の飽和昇華圧状態に置くための密閉可能な真空容器 J 1 と、真空容器 C 1 と真空容器 J 1 とを相互に連結させる接続配管と、前記接続配管の開閉機構と、真空容器 C 1 内の圧力を独立して調節する排気系と、真空容器 J 1 内の圧力を独立して調節する排気系と、前記有機化合物が昇華して有機化合物の蒸気が前記樹脂成形物表面に付着した後、更に前記有機化合物が前記樹脂成形物中に浸透・分散するための加熱手段と、を設けたことを特徴とする樹脂表面層の改質装置。

【請求項 19】 請求項 16、請求項 17、または、請

求項 18 に記載の樹脂表面層の改質装置であって、粉末状の前記樹脂成形物を攪拌するための機構を設けたことを特徴とする樹脂表面層の改質装置。

【請求項 20】 請求項 16、請求項 17、または、請求項 18 に記載の樹脂表面層の改質装置であって、繊維状、ファイバー状、またはフィルム状の中から選択される形態の前記樹脂成形物を減圧状態下で、供給側リールから受側リールへ巻き取るための機構を設けたことを特徴とする樹脂表面層の改質装置。

【請求項 21】 昇華性を有しかつ着色される樹脂成形物の樹脂と親和性を有する色素、および、前記樹脂成形物を、前記色素の飽和昇華圧状態に置くための密閉可能な容器と、前記密閉可能な容器の圧力を調整するための排気系と、前記色素が昇華して色素の蒸気が前記樹脂成形物表面に付着した後、更に前記色素が前記樹脂成形物中に浸透・分散するための加熱手段と、を設けたことを特徴とする樹脂表面層の着色装置。

【請求項 22】 請求項 21 に記載の樹脂成形物表面層の着色装置であって、更に、前記色素が、前記樹脂成形物表面に付着可能なように、上記 5 つの態様からなる群の中から選択される少なくとも 1 つの態様で、保持されるための昇華源基板を設けたことを特徴とする樹脂表面層の着色装置。

【請求項 23】 昇華性を有しかつ着色される樹脂成形物の樹脂と親和性を有する色素を、飽和昇華圧状態に置くための密閉可能な真空容器 C 1 と、前記樹脂成形物を、前記色素の飽和昇華圧状態に置くための密閉可能な真空容器 J 1 と、真空容器 C 1 と真空容器 J 1 とを相互に連結させる接続配管と、前記接続配管の開閉機構と、真空容器 C 1 内の圧力を独立して調節する排気系と、真空容器 J 1 内の圧力を独立して調節する排気系と、前記色素が昇華して色素の蒸気が前記樹脂成形物表面に付着した後、更に前記色素が前記樹脂成形物中に浸透・分散するための加熱手段と、を設けたことを特徴とする樹脂表面層の着色装置。

【請求項 24】 請求項 21、請求項 22、または、請求項 23 に記載の樹脂表面層の着色装置であって、粉末状の前記樹脂成形物を攪拌するための機構を設けたことを特徴とする樹脂表面層の着色装置。

【請求項 25】 請求項 21、請求項 22、または、請求項 23 に記載の樹脂表面層の着色装置であって、繊維状、ファイバー状、またはフィルム状の中から選択される形態の前記樹脂成形物を減圧状態下で、供給側リールから受側リールへ巻き取るための機構を設けたことを特徴とする樹脂表面層の着色装置。

【請求項 26】 請求項 1、請求項 2、請求項 3、請求項 4、請求項 5、請求項 6、請求項 7、請求項 8、請求



項9、請求項10、請求項11、または、請求項12に記載の樹脂表面層の改質方法によって、表面層が改質されたことを特徴とする樹脂形成物。

【請求項27】 請求項13に記載の樹脂表面層の改質方法によって、表面層が改質されたことを特徴とする樹脂形成物。

【請求項28】 請求項14に記載の樹脂表面層の着色方法によって、表面層が着色されたことを特徴とする樹脂形成物。

【請求項29】 請求項15に記載の樹脂表面層の着色方法によって、表面層が着色されたことを特徴とする樹脂形成物。

【請求項30】 請求項1、請求項2、請求項3、請求項4、請求項5、請求項6、請求項7、請求項8、請求項9、請求項10、請求項11、または、請求項12に記載の樹脂表面層の改質方法によって、表面層が改質されたことを特徴とするプラスチックレンズ。

【請求項31】 請求項14に記載の樹脂表面層の着色方法によって、表面層が着色されたことを特徴とするプラスチックレンズ。

【請求項32】 請求項1、請求項2、請求項3、請求項4、請求項5、請求項6、請求項7、請求項8、請求項9、請求項10、請求項11、または、請求項12に記載の樹脂表面層の改質方法によって、樹脂表面層が改質されたことを特徴とする樹脂コートレンズ。

【請求項33】 請求項14に記載の樹脂表面層の着色方法によって、樹脂表面層が着色されたことを特徴とする樹脂コートレンズ。

【請求項34】 請求項1、請求項2、請求項3、請求項4、請求項5、請求項6、請求項7、請求項8、請求項9、請求項10、請求項11、または、請求項12に記載の樹脂表面層の改質方法によって、表面層が改質されたことを特徴とするプラスチックフィルム。

【請求項35】 請求項14に記載の樹脂表面層の着色方法によって、表面層が着色されたことを特徴とするプラスチックフィルム。

【請求項36】 請求項1、請求項2、請求項3、請求項4、請求項5、請求項6、請求項7、請求項8、請求項9、請求項10、請求項11、または、請求項12に記載の樹脂表面層の改質方法によって、表面層が改質されたことを特徴とする繊維。

【請求項37】 請求項14に記載の樹脂表面層の着色方法によって、表面層が着色されたことを特徴とする繊維。

【請求項38】 請求項1、請求項2、請求項3、請求項4、請求項5、請求項6、請求項7、請求項8、請求項9、請求項10、請求項11、または、請求項12に記載の樹脂表面層の改質方法によって、表面層が改質されたことを特徴とするプラスチック光ファイバー。

【請求項39】 請求項14に記載の樹脂表面層の着色

方法によって、表面層が着色されたことを特徴とするプラスチック光ファイバー。

【請求項40】 請求項1、請求項2、請求項3、請求項4、請求項5、請求項6、請求項7、請求項8、請求項9、請求項10、請求項11、または、請求項12に記載の樹脂表面層の改質方法、および、昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する蛍光色素を用いた表面層改質によって、表面層が蛍光発光機能を付与されたことを特徴とする樹脂形成物。

【請求項41】 請求項1、請求項2、請求項3、請求項4、請求項5、請求項6、請求項7、請求項8、請求項9、請求項10、請求項11、または、請求項12に記載の樹脂表面層の改質方法、および、昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有するフォトクロミック色素を用いた表面層改質によって、表面層がフォトクロミック機能を付与されたことを特徴とする樹脂形成物。

【請求項42】 請求項1、請求項2、請求項3、請求項4、請求項5、請求項6、請求項7、請求項8、請求項9、請求項10、請求項11、または、請求項12に記載の樹脂表面層の改質方法、および、昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する有機金属化合物を用いた表面層改質によって、表面層がX線および/または電子線および/または放射線吸収機能を付与されたことを特徴とする樹脂形成物。

【請求項43】 請求項1、請求項2、請求項3、請求項4、請求項5、請求項6、請求項7、請求項8、請求項9、請求項10、請求項11、または、請求項12に記載の樹脂表面層の改質方法、および、昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する抗菌防カビ剤を用いた表面層改質によって、表面層が抗菌防カビ機能を付与されたことを特徴とする樹脂形成物。

【請求項44】 請求項1、請求項2、請求項3、請求項4、請求項5、請求項6、請求項7、請求項8、請求項9、請求項10、請求項11、または、請求項12に記載の樹脂表面層の改質方法、および、昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する薬理活性有機化合物を用いた表面層改質によって、表面層が薬理活性機能を付与されたことを特徴とする樹脂形成物。

【請求項45】 請求項1、請求項2、請求項3、請求項4、請求項5、請求項6、請求項7、請求項8、請求項9、請求項10、請求項11、または、請求項12に記載の樹脂表面層の改質方法、および、昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有し、動植物に対して生理活性を示す有機化合物を用いた表面層改質によって、表面層が農薬としての機能を付与されたことを特徴とする樹脂形成物。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 この発明は、樹脂成形物表面

層の改質方法およびそのための装置および表面層が改質された樹脂成形物、および樹脂成形物表面層の着色方法およびそのための装置および表面層が着色された樹脂成形物、および表面層の改質により機能性を付与された樹脂成形物に関するものである。

#### 【0002】

【従来の技術】【樹脂表面層の改質方法】樹脂成形物の改質方法としては、例えば、X線やガンマ線などの電磁波を照射する方法が知られている。しかしながら、樹脂成形物の表面からある深さにわたる「表面層」のみを改質し、樹脂成形物の内部については改質しない改質方法はごく限られているだけでなく、多くの制約を伴っている。

【0003】例えば、樹脂表面に金属や有機化合物のイオンビームを打ち込む方法が知られているが、大面積の樹脂フィルム全体を均一に処理することが難しい、複雑な形状の樹脂成形物の表面全体を均一に処理することが難しい、イオンビームとして使用できる有機化合物が制限される、などの制約がある。

【0004】例えば、樹脂表面に高パワー密度のレーザーパルスで短時間照射して表面を改質する方法（レーザーアブレーション法）が知られているが、大面積の樹脂フィルム全体を均一に処理することが難しい、複雑な形状の樹脂成形物の表面全体を均一に処理することが難しい、などの制約がある。

【0005】例えば、樹脂表面を大気圧下、プラズマ処理して表面を酸化・改質する方法が知られているが、酸化し難い表面には適用できない、効果が長続きしない、などの制約がある。

【0006】樹脂表面層を改質するための処理剤が液体の場合、樹脂成形物の表面に塗工することができ、一方、固体の場合は、適当な溶媒を用い溶液として塗工することや、溶液中に樹脂成形物を浸ける方法を取ることができる。しかしながら、このような湿式の方法は、樹脂表面の平滑性や微細構造が失われやすい、樹脂表面に過剰の処理剤が残らないようにするためには洗浄が必要である、洗浄の際に表面処理の効果が損なわれるおそれがある、溶剤を用いる場合、樹脂表面が溶剤で膨潤するおそれがある、などの制約がある。

【0007】また、樹脂表面層を改質するための処理剤を樹脂全体に混合・混練して成形する方法も広く用いられているが、本来ならば表面層にのみ必要な処理剤を樹脂全体に混合する必要がある、樹脂全体に混合した処理剤が樹脂の物性に悪影響を及ぼす場合がある、樹脂全体に混合した処理剤が樹脂の物性に悪影響を与えないようにするため必要充分量を添加できない、樹脂全体に混合する処理剤の種類に制約がある、などの問題がある。

【0008】【樹脂成形物表面の着色方法】樹脂成形物の着色方法としては、例えば、樹脂中に染料または顔料を混練した後、（１）射出成形して着色された樹脂成形

物を得る方法、（２）延伸して着色されたフィルム状のものを得る方法、（３）紡糸して繊維状のものを得る方法などが広く用いられている。

【0009】一方、樹脂成形物の内部の組成を変えずに、表面のみを着色する方法としては、各種の塗工法や印刷法が広く用いられている。

【0010】樹脂表面層に浸透する性質の色素のみを、塗工法や印刷法で樹脂成形物表面に付着させ、浸透させるような特殊な方法の場合を除き、通常の塗工法や印刷法の場合、バインダー樹脂と染料または顔料の混合物からなる層が樹脂表面に形成される。厳密に言う、このような着色方法は「表面そのものの着色」ではなく、「着色された膜を表面に追加し、付着させること」である。従って、樹脂表面に微細加工がなされている場合、追加された膜によって微細加工が埋没してしまう、と言う問題がある。また、塗工法を用いる場合、樹脂成形物表面の平滑性などが、塗工溶剤による溶解や膨潤によって損なわれるおそれがある。そこで、樹脂表面層の溶解や膨潤を避けようとする、適当な塗工溶剤が見つからず、塗工法の適用が困難になる場合がある。例えば、ポリ（メタクリル酸メチル）からなる樹脂成形物の表面に、色素とポリ（メタクリル酸メチル）からなる膜を溶剤を用いた塗工法で作製しようとする、ポリ（メタクリル酸メチル）を溶解する溶剤は必ず、ポリ（メタクリル酸メチル）からなる樹脂成形物の表面を浸食してしまい、平滑な塗工面を得ることは容易でない。

【0011】樹脂表面に昇華性の色素を含有する塗工膜または印刷膜を付着させて着色しようとする場合、更に、次のような問題がある。

【0012】（i）昇華性色素と樹脂からなる組成物を塗工しない印刷する場合、工程の途中で昇華性色素が昇華してしまうことがある。このため、組成を一定にするための制御および組成を均一化するための制御が容易でない。

【0013】（ii）昇華性色素のみを残留させて、その他の揮発性不純物を除去することは極めて困難である。従って、昇華性色素以外の揮発性不純物を含まない塗工膜・印刷膜を作製することが容易でない。

【0014】樹脂表面に塗工膜や印刷膜を形成する方法の他に、昇華性色素の蒸着膜を形成し、樹脂成形物の着色を行うこともできる。通常の蒸着法では、蒸着源の温度を被成膜基板の温度よりも高くして、蒸着源から飛来した有機化合物蒸気をより低温の被成膜基板表面に堆積させる。このような非平衡条件下の成膜方法において、膜厚制御はもっぱら機械的手段によって行われる。すなわち、蒸着源から被成膜基板に至る空間に、マスクまたはスリットを設置し、有機化合物蒸気の濃度を空間的に制御し、また、被成膜基板を回転させるなどを行い、蒸着膜の膜厚の均一化を図っている。しかしながら、有機化合物（色素）の蒸気圧が高くて昇華しやすい場合、こ

のような機械的手段だけで蒸着膜の膜厚を均一にすることは容易でない。

【0015】昇華を用いた画像印刷方法として昇華転写法が知られている。すなわち、昇華転写リボンまたはシートの表面に成膜された昇華性色素を、加熱ヘッドで加熱して昇華させ、近傍に置かれた紙表面の転写層（熱可塑性樹脂からなる薄膜）へ堆積・浸透させる方法である。原理的には蒸着法と同等であり、画像の濃淡は加熱ヘッドにおける加熱面積および加熱量によって制御される。従って、「点描画」の原理で、微細な階調のある画像を印刷する用途には適しているが、大面積について均一な濃度で樹脂表面の着色を行うには不適当である。また、複雑な表面形状の樹脂成形物の着色にも向かない。

【0016】

【発明が解決しようとする課題】この発明は以上のような課題を解決し、（a）昇華性有機化合物と樹脂からなり、これらの組成が均一な、改質された表面層を樹脂成形物の表面に作製する方法、（b）昇華性有機化合物を含有し、かつ、揮発性の不純物を含まない、改質された表面層を樹脂成形物の表面に作製する方法、（c）昇華性有機化合物と樹脂からなり、これらの組成が均一な、改質された表面層を樹脂成形物の表面に効率よく作製する方法、（d）樹脂成形物の表面平滑性を損なわずに、昇華性有機化合物を含有した、改質された表面層を樹脂成形物の表面に作製する方法、（e）樹脂成形物の表面に微細加工が施されている場合、この表面構造を損なわずに、昇華性有機化合物を含有した、改質された表面層を樹脂成形物の表面に作製する方法、（f）広範な種類の昇華性有機化合物を含有した、改質された表面層を樹脂成形物の表面に作製する方法、（g）複雑な機械的制御なしに、膜厚および／または組成が均一な昇華性有機化合物を含有した、改質された表面層を樹脂成形物の表面に作製する方法、（h）表面層の面積の大小に関わらず、均一な膜厚および／または組成を有する昇華性有機化合物を含有した、改質された表面層を樹脂成形物の表面に作製する方法、（i）上記（a）～（h）の特徴を有する改質された表面層を樹脂成形物の表面に作製するための装置、（j）上記（a）～（h）の特徴を有する改質された表面層を持つ樹脂成形物、（k）昇華性色素と樹脂からなり、これらの組成が均一な、着色された表面層を樹脂成形物の表面に作製する方法、（l）昇華性色素を含有し、かつ、揮発性の不純物を含まない、着色された表面層を樹脂成形物の表面に作製する方法、

（m）昇華性色素と樹脂からなり、これらの組成が均一な、着色された表面層を樹脂成形物の表面に効率よく作製する方法、（n）樹脂成形物の表面平滑性を損なわずに、昇華性色素を含有した、着色された表面層を樹脂成形物の表面に作製する方法、（o）樹脂成形物の表面に微細加工が施されている場合、この表面構造を損なわずに、昇華性色素を含有した、着色された表面層を樹脂成

形物の表面に作製する方法、（p）広範な種類の昇華性色素を含有した、着色された表面層を樹脂成形物の表面に作製する方法、（q）複雑な機械的制御なしに、膜厚および／または組成が均一な昇華性色素を含有した、着色された表面層を樹脂成形物の表面に作製する方法、

（r）表面層の面積の大小に関わらず、均一な膜厚および／または組成を有する昇華性色素を含有した、着色された表面層を樹脂成形物の表面に作製する方法、（s）上記（k）～（r）の特徴を有する着色された表面層を樹脂成形物の表面に作製するための装置、（t）上記（k）～（r）の特徴を有する着色された表面層を持つ樹脂成形物、（u）表面層が改質されたことによって、表面層が機能性を付与された樹脂成形物、を提供することを目的とする。

【0017】

【課題を解決するための手段】上記目的を達成するために、本願の請求項1記載の発明に係る樹脂成形物表面層の改質方法は、昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する有機化合物と、前記樹脂成形物とを、閉じた空間内に載置し、前記閉じた空間内を前記有機化合物の飽和昇華圧状態に置き、前記有機化合物蒸気を前記樹脂成形物表面に均一に付着させ、付着した前記有機化合物を前記樹脂成形物表面から内部に浸透・分散させることを特徴とする。

【0018】ここで、飽和昇華圧とは、飽和蒸気圧とも呼ばれ、熱力学系のある一定の温度における蒸気圧であって、物質の固相の表面で、物質の蒸気圧が平衡状態にあることを言う。飽和蒸気圧は、物質の量に依存せず、温度のみに依存し、温度の上昇とともに単調に増加する。その変化の様子は、以下に示すクラウジスークラペイロン（Clausius-Clapeyron）の式で示される。

【0019】

【数1】

$$dp/dT = Q/T \Delta V \quad \dots (1)$$

ここで、Qは単位質量の物質（固体）が気体（蒸気）になるときに吸収する熱量（昇華熱；この熱量吸収によって物質の温度は上昇しない）を、 $\Delta V$ は固体から気体への相変化における単位質量当たりの体積の差を、pは飽和蒸気圧を、Tは温度を表す。

【0020】上記目的を達成するために、また、本願の請求項2記載の発明に係る樹脂成形物表面層の改質方法は、昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する有機化合物を閉じた空間C内に載置し、一方、前記樹脂成形物を閉じた空間J内に載置し、閉じた空間J内の温度を、閉じた空間C内の温度と同一または閉じた空間C内の温度よりも高く制御し、閉じた空間C内の圧力を前記有機化合物の飽和昇華圧状態に置き、閉じた空間J内の圧力を、閉じた空間C内の圧力と同一または閉じた空間C内の圧力よりも低く制御し、次いで、閉じた空間Cと閉じた空間Jとを連結させて、閉じた空

間Cと閉じた空間Jとを合わせた閉じた空間Mとし、更に、閉じた空間M内全体が前記有機化合物の飽和昇華圧状態になるよう温度および圧力を制御し、連結前の閉じた空間C内に充満した前記有機化合物の蒸気が連結前の閉じた空間J内に拡散するようにし、前記有機化合物蒸気を前記樹脂成形物表面に均一に付着させ、付着した前記有機化合物を前記樹脂成形物表面から内部に浸透・分散させることを特徴とする。

【0021】上記目的を達成するために、また、本願の請求項3記載の発明に係る樹脂成形物表面層の改質方法は、請求項1に記載の樹脂成形物表面層の改質方法において、前記有機化合物は、前記樹脂成形物表面に付着可能なように、以下の(A)～(E)の5つの態様からなる群の中から選択される少なくとも1つの態様で、昇華源基板に付着または含有されていることを特徴とする。

【0022】(A)前記有機化合物が単独で昇華源基板の表面に塗工または成膜されている、(B)前記有機化合物とバインダー樹脂とが昇華源基板の表面に塗工または成膜されている、(C)前記有機化合物を含浸している多孔質粒子が昇華源基板の表面に塗工または成膜されている、(D)前記有機化合物を含浸している多孔質粒子とバインダー樹脂とが昇華源基板の表面に塗工または成膜されている、(E)多孔性の昇華源基板表面の孔に前記有機化合物が含浸されたもの。

【0023】上記目的を達成するために、また、本願の請求項4記載の発明に係る樹脂成形物表面層の改質方法は、請求項3に記載の樹脂表面層の改質方法において、上記(A)～(E)のいずれかの態様でその表面に前記有機化合物を付着または含有する前記昇華源基板の表面を前記樹脂成形物表面の近傍に配置することを特徴とする。

【0024】ここで、「近傍」とは前記昇華源基板の表面と前記樹脂成形物表面とが接触しない限りにおいて、できる限り接近させることを意味する。例えば、前記昇華源基板および前記樹脂成形物表面ともに表面の凹凸が1 $\mu$ m未満の平滑平面であったとすれば、平面間の距離をマイクロメートルオーダーで接近させることが至適である。ただし、表面層改質・着色処理時の操作の容易性を考慮すると、これを下限として、数ミリメートルないし10ミリメートル程度まで接近させることが好ましい。

【0025】上記目的を達成するために、また、本願の請求項5記載の発明に係る樹脂成形物表面層の改質方法は、請求項1に記載の樹脂表面層の改質方法において、前記樹脂成形物および前記有機化合物を真空容器に入れ、前記真空容器に設けられた真空弁から排気して前記真空容器内の圧力を、室温以上であって前記有機化合物および／または前記樹脂の熱分解温度を越えない温度における前記有機化合物の飽和昇華圧まで減圧し、前記真空容器に設けられた真空弁をすべて密閉して閉じた空間

とし、密閉された前記真空容器内部の温度を、上記減圧状態において前記有機化合物の分圧が飽和昇華圧に到達する温度まで加熱し、所定時間加熱後、前記真空容器を徐冷することを特徴とする。

【0026】上記目的を達成するために、また、本願の請求項6記載の発明に係る樹脂成形物表面層の改質方法は、請求項3に記載の樹脂表面層の改質方法において前記請求項3に記載のいずれかの態様で昇華源基板に付着または含有された前記有機化合物および前記樹脂成形物を、真空容器に入れ、前記真空容器に設けられた真空弁から排気して前記真空容器内の圧力を、室温以上であって前記有機化合物および／または前記樹脂の熱分解温度を越えない温度における前記有機化合物の飽和昇華圧まで減圧し、前記真空容器に設けられた真空弁をすべて密閉して閉じた空間とし、密閉された前記真空容器内部の温度を、上記減圧状態において前記有機化合物の分圧が飽和昇華圧に到達する温度まで加熱し、所定時間加熱後、前記真空容器を徐冷することを特徴とする。

【0027】上記目的を達成するために、また、本願の請求項7記載の発明に係る樹脂成形物表面層の改質方法は、請求項4に記載の樹脂表面層の改質方法において、前記請求項3に記載のいずれかの態様で昇華源基板に付着または含有された前記有機化合物および前記樹脂成形物を、真空容器に入れ、前記真空容器に設けられた真空弁から排気して前記真空容器内の圧力を、室温以上であって前記有機化合物および／または前記樹脂の熱分解温度を越えない温度における前記有機化合物の飽和昇華圧まで減圧し、前記真空容器に設けられた真空弁をすべて密閉して閉じた空間とし、密閉された前記真空容器内部の温度を、上記減圧状態において前記有機化合物の分圧が飽和昇華圧に到達する温度まで加熱し、所定時間加熱後、徐冷することを特徴とする。

【0028】上記目的を達成するために、また、本願の請求項8記載の発明に係る樹脂成形物表面層の改質方法は、請求項1に記載の樹脂表面層の改質方法において、前記樹脂成形物および前記有機化合物を真空容器に入れ、前記真空容器内部の温度を室温以上であって、前記有機化合物および／または前記樹脂の熱分解温度を越えない温度まで加熱し、上記温度に保ちながら、前記真空容器に設けられた真空弁から排気して前記真空容器内の圧力を、上記温度における前記有機化合物の飽和昇華圧まで減圧し、前記真空容器に設けられた真空弁をすべて密閉して閉じた空間とし、所定時間加熱減圧後、前記真空容器を徐冷することを特徴とする。

【0029】上記目的を達成するために、また、本願の請求項9記載の発明に係る樹脂成形物表面層の改質方法は、請求項3に記載の樹脂表面層の改質方法において、前記請求項3に記載のいずれかの態様で昇華源基板に付着または含有された前記有機化合物および前記樹脂成形物を、真空容器に入れ、前記真空容器内部の温度を室温

以上であって、前記有機化合物および／または前記樹脂の熱分解温度を越えない温度まで加熱し、上記温度に保ちながら、前記真空容器に設けられた真空弁から排気して前記真空容器内の圧力を、上記温度における前記有機化合物の飽和昇華圧まで減圧し、前記真空容器に設けられた真空弁をすべて密閉して閉じた空間とし、所定時間加熱減圧後、前記真空容器を徐冷することを特徴とする。

【0030】上記目的を達成するために、また、本願の請求項10記載の発明に係る樹脂成形物表面層の改質方法は、請求項4に記載の樹脂表面層の改質方法において、前記請求項3に記載のいずれかの態様で昇華源基板に付着または含有された前記有機化合物および前記樹脂成形物を、真空容器に入れ、前記真空容器内部の温度を室温以上であって、前記有機化合物および／または前記樹脂の熱分解温度を越えない温度まで加熱し、上記温度に保ちながら、前記真空容器に設けられた真空弁から排気して前記真空容器内の圧力を、上記温度における前記有機化合物の飽和昇華圧まで減圧し、前記真空容器に設けられた真空弁をすべて密閉して閉じた空間とし、所定時間加熱減圧後、前記真空容器を徐冷することを特徴とする。

【0031】上記目的を達成するために、また、本願の請求項11記載の発明に係る樹脂成形物表面層の改質方法は、請求項2に記載の樹脂表面層の改質方法において、昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する有機化合物を、排気系への配管および前記有機化合物導入部および真空容器J1への接続配管を設けた真空容器C1に入れ、前記有機化合物導入部および真空容器J1への接続配管を閉じてから前記排気系より真空容器C1内の圧力を、室温以上であって前記有機化合物および／または前記樹脂の熱分解温度を越えない温度における前記有機化合物の飽和昇華圧まで減圧し、真空容器C1内の温度を前記温度まで加熱し、一方、前記樹脂成形物を、排気系への配管および前記樹脂成形物導入部および真空容器C1への接続配管を設けた真空容器J1に入れ、前記樹脂成形物導入部および真空容器C1への接続配管を閉じ、真空容器J1内の温度を、真空容器C1内の温度と同一または真空容器C1内の温度よりも高く制御し、真空容器C1内の圧力を前記有機化合物の飽和昇華圧状態に置き、真空容器J1内の圧力を、真空容器C1内の圧力と同一または真空容器C1内の圧力よりも低く制御し、次いで、真空容器C1と真空容器J1とを相互の接続配管を通じて連結させて、真空容器C1内の閉じた空間Cと真空容器J1内の閉じた空間Jとを合わせた閉じた空間Mとし、更に、閉じた空間M内全体が前記有機化合物の飽和昇華圧状態になるよう温度および圧力を制御し、連結前の真空容器C1内に充満した前記有機化合物の蒸気が連結前の真空容器J1内に拡散するようにし、前記有機化合物蒸気を前記樹脂成形物表

面に均一に付着させ、付着した前記有機化合物を前記樹脂成形物表面から内部に浸透・分散させるため所定時間加熱した後、真空容器C1と真空容器J1とを相互に連結している接続配管を閉じ、真空容器J1内部に残留している前記有機化合物の蒸気が前記樹脂成形物表面から内部に浸透・分散するよう真空容器J1内の温度および圧力を所定時間制御し、真空容器J1内部に前記有機化合物の蒸気が過剰に存在している場合は排気系から真空容器J1外部へ排出し、次いで、真空容器J1内の前記樹脂成形物の温度を常温へ戻すことを特徴とする。

【0032】上記目的を達成するために、また、本願の請求項12記載の発明に係る樹脂成形物表面層の改質方法は、請求項11に記載の樹脂表面層の改質方法において、最終段階で真空容器J1内の前記樹脂成形物の温度を常温へ戻す替わりに、ゲート弁を通じて真空容器J1に隣接して設けられ、独立して圧力制御可能な真空容器J2内へ、前記樹脂成形物を減圧下で移送してから前記樹脂成形物の温度を常温へ戻すことを特徴とする。

【0033】上記目的を達成するために、また、本願の請求項13記載の発明に係る樹脂成形物表面層の改質方法は、請求項5、請求項6、請求項7、請求項8、請求項9、請求項10、請求項11、または、請求項12に記載の樹脂表面層の改質方法において、前記有機化合物蒸気を前記樹脂成形物表面に均一に付着させ、付着した前記有機化合物を前記樹脂成形物表面から内部に浸透・分散させるために、前記樹脂成形物の温度を前記樹脂のガラス転移温度以上であって、前記有機化合物および／または前記樹脂の熱分解温度を越えない温度まで加熱することを特徴とする。

【0034】上記目的を達成するために、また、本願の請求項14記載の発明に係る樹脂成形物表面層の着色方法は、請求項1、請求項2、請求項3、請求項4、請求項5、請求項6、請求項7、請求項8、請求項9、請求項10、請求項11、または、請求項12に記載の樹脂表面層の改質方法において、前記有機化合物として、昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する色素を用いることによって前記樹脂成形物の表面層を改質すると同時に着色することを特徴とする。

【0035】上記目的を達成するために、また、本願の請求項15記載の発明に係る樹脂成形物表面層の着色方法は、請求項13に記載の樹脂表面層の改質方法において、前記有機化合物として、昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する色素を用いることによって前記樹脂成形物の表面層を改質すると同時に着色することを特徴とする。

【0036】上記目的を達成するために、また、本願の請求項16記載の発明に係る樹脂成形物表面層の改質装置は、昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する有機化合物、および、前記樹脂成形物を、前記有機化合物の飽和昇華圧状態に置くための密閉

可能な容器と、前記密閉可能な容器の圧力を調整するための排気系と、前記有機化合物が昇華して有機化合物の蒸気が前記樹脂成形物表面に付着した後、更に前記有機化合物が前記樹脂成形物中に浸透・分散するための加熱手段と、を設けたことを特徴とする。

【0037】上記目的を達成するために、また、本願の請求項17記載の発明に係る樹脂成形物表面層の改質装置は、請求項16に記載の樹脂成形物表面層の改質装置であって、更に、前記有機化合物が、前記樹脂成形物表面に付着可能なように、上記5つの態様からなる群の中から選択される少なくとも1つの態様で、保持されるための昇華源基板を設けたことを特徴とする。

【0038】上記目的を達成するために、また、本願の請求項18記載の発明に係る樹脂成形物表面層の改質装置は、昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する有機化合物を、飽和昇華圧状態に置くための密閉可能な真空容器C1と、前記樹脂成形物を、前記有機化合物の飽和昇華圧状態に置くための密閉可能な真空容器J1と、真空容器C1と真空容器J1とを相互に連結させる接続配管と、前記接続配管の開閉機構と、真空容器C1内の圧力を独立して調節する排気系と、真空容器J1内の圧力を独立して調節する排気系と、前記有機化合物が昇華して有機化合物の蒸気が前記樹脂成形物表面に付着した後、更に前記有機化合物が前記樹脂成形物中に浸透・分散するための加熱手段と、を設けたことを特徴とする。

【0039】上記目的を達成するために、また、本願の請求項19記載の発明に係る樹脂成形物表面層の改質装置は、請求項16、請求項17、または、請求項18に記載の樹脂表面層の改質装置であって、粉末状の前記樹脂成形物を攪拌するための機構を設けたことを特徴とする。

【0040】上記目的を達成するために、また、本願の請求項20記載の発明に係る樹脂成形物表面層の改質装置は、請求項16、請求項17、または、請求項18に記載の樹脂表面層の改質装置であって、繊維状、ファイバー状、またはフィルム状の中から選択される形態の前記樹脂成形物を減圧状態で、供給側リールから受側リールへ巻き取るための機構を設けたことを特徴とする。

【0041】上記目的を達成するために、また、本願の請求項21記載の発明に係る樹脂成形物表面層の着色装置は、昇華性を有しかつ着色される樹脂成形物の樹脂と親和性を有する色素、および、前記樹脂成形物を、前記色素の飽和昇華圧状態に置くための密閉可能な容器と、前記密閉可能な容器の圧力を調整するための排気系と、前記色素が昇華して色素の蒸気が前記樹脂成形物表面に付着した後、更に前記色素が前記樹脂成形物中に浸透・分散するための加熱手段と、を設けたことを特徴とする。

【0042】上記目的を達成するために、また、本願の

請求項22記載の発明に係る樹脂成形物表面層の着色装置は、請求項21に記載の樹脂成形物表面層の着色装置であって、更に、前記色素が、前記樹脂成形物表面に付着可能なように、上記5つの態様からなる群の中から選択される少なくとも1つの態様で、保持されるための昇華源基板を設けたことを特徴とする。

【0043】上記目的を達成するために、また、本願の請求項23記載の発明に係る樹脂成形物表面層の着色装置は、昇華性を有しかつ着色される樹脂成形物の樹脂と親和性を有する色素を、飽和昇華圧状態に置くための密閉可能な真空容器C1と、前記樹脂成形物を、前記色素の飽和昇華圧状態に置くための密閉可能な真空容器J1と、真空容器C1と真空容器J1とを相互に連結させる接続配管と、前記接続配管の開閉機構と、真空容器C1内の圧力を独立して調節する排気系と、真空容器J1内の圧力を独立して調節する排気系と、前記色素が昇華して色素の蒸気が前記樹脂成形物表面に付着した後、更に前記色素が前記樹脂成形物中に浸透・分散するための加熱手段と、を設けたことを特徴とする。

【0044】上記目的を達成するために、また、本願の請求項24記載の発明に係る樹脂成形物表面層の着色装置は、請求項21、請求項22、または、請求項23に記載の樹脂表面層の着色装置であって、粉末状の前記樹脂成形物を攪拌するための機構を設けたことを特徴とする。

【0045】上記目的を達成するために、また、本願の請求項25記載の発明に係る樹脂成形物表面層の着色装置は、請求項21、請求項22、または、請求項23に記載の樹脂表面層の着色装置であって、繊維状、ファイバー状、またはフィルム状の中から選択される形態の前記樹脂成形物を減圧状態で、供給側リールから受側リールへ巻き取るための機構を設けたことを特徴とする。

【0046】上記目的を達成するために、また、本願の請求項26記載の発明に係る樹脂成形物は、請求項1、請求項2、請求項3、請求項4、請求項5、請求項6、請求項7、請求項8、請求項9、請求項10、請求項11、または、請求項12に記載の樹脂表面層の改質方法によって、表面層が改質されたことを特徴とする。

【0047】上記目的を達成するために、また、本願の請求項27記載の発明に係る樹脂成形物は、請求項13に記載の樹脂表面層の改質方法によって、表面層が改質されたことを特徴とする。

【0048】上記目的を達成するために、また、本願の請求項28記載の発明に係る樹脂成形物は、請求項14に記載の樹脂表面層の着色方法によって、表面層が着色されたことを特徴とする。

【0049】上記目的を達成するために、また、本願の請求項29記載の発明に係る樹脂成形物は、請求項15に記載の樹脂表面層の着色方法によって、表面層が着色されたことを特徴とする。

【0050】上記目的を達成するために、また、本願の請求項30記載の発明に係るプラスチックレンズは、請求項1、請求項2、請求項3、請求項4、請求項5、請求項6、請求項7、請求項8、請求項9、請求項10、請求項11、または、請求項12に記載の樹脂表面層の改質方法によって、表面層が改質されたことを特徴とする。

【0051】上記目的を達成するために、また、本願の請求項31記載の発明に係るプラスチックレンズは、請求項14に記載の樹脂表面層の着色方法によって、表面層が着色されたことを特徴とする。

【0052】上記目的を達成するために、また、本願の請求項32記載の発明に係る樹脂コートレンズは、請求項1、請求項2、請求項3、請求項4、請求項5、請求項6、請求項7、請求項8、請求項9、請求項10、請求項11、または、請求項12に記載の樹脂表面層の改質方法によって、樹脂表面層が改質されたことを特徴とする。

【0053】上記目的を達成するために、また、本願の請求項33記載の発明に係る樹脂コートレンズは、請求項14に記載の樹脂表面層の着色方法によって、樹脂表面層が着色されたことを特徴とする。

【0054】上記目的を達成するために、また、本願の請求項34記載の発明に係るプラスチックフィルムは、請求項1、請求項2、請求項3、請求項4、請求項5、請求項6、請求項7、請求項8、請求項9、請求項10、請求項11、または、請求項12に記載の樹脂表面層の改質方法によって、表面層が改質されたことを特徴とする。

【0055】上記目的を達成するために、また、本願の請求項35記載の発明に係るプラスチックフィルムは、請求項14に記載の樹脂表面層の着色方法によって、表面層が着色されたことを特徴とする。

【0056】上記目的を達成するために、また、本願の請求項36記載の発明に係る繊維は、請求項1、請求項2、請求項3、請求項4、請求項5、請求項6、請求項7、請求項8、請求項9、請求項10、請求項11、または、請求項12に記載の樹脂表面層の改質方法によって、表面層が改質されたことを特徴とする。

【0057】上記目的を達成するために、また、本願の請求項37記載の発明に係る繊維は、請求項14に記載の樹脂表面層の着色方法によって、表面層が着色されたことを特徴とする。

【0058】上記目的を達成するために、また、本願の請求項38記載の発明に係るプラスチック光ファイバーは、請求項1、請求項2、請求項3、請求項4、請求項5、請求項6、請求項7、請求項8、請求項9、請求項10、請求項11、または、請求項12に記載の樹脂表面層の改質方法によって、表面層が改質されたことを特徴とする。

【0059】上記目的を達成するために、また、本願の請求項39記載の発明に係るプラスチック光ファイバーは、請求項14に記載の樹脂表面層の着色方法によって、表面層が着色されたことを特徴とする。

【0060】上記目的を達成するために、また、本願の請求項40記載の発明に係る樹脂成形物は、請求項1、請求項2、請求項3、請求項4、請求項5、請求項6、請求項7、請求項8、請求項9、請求項10、請求項11、または、請求項12に記載の樹脂表面層の改質方法、および、昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する蛍光色素を用いた表面層改質によって、表面層が蛍光発光機能を付与されたことを特徴とする。

【0061】上記目的を達成するために、また、本願の請求項41記載の発明に係る樹脂成形物は、請求項1、請求項2、請求項3、請求項4、請求項5、請求項6、請求項7、請求項8、請求項9、請求項10、請求項11、または、請求項12に記載の樹脂表面層の改質方法、および、昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有するフォトリソミック色素を用いた表面層改質によって、表面層がフォトリソミック機能を付与されたことを特徴とする。

【0062】上記目的を達成するために、また、本願の請求項42記載の発明に係る樹脂成形物は、請求項1、請求項2、請求項3、請求項4、請求項5、請求項6、請求項7、請求項8、請求項9、請求項10、請求項11、または、請求項12に記載の樹脂表面層の改質方法、および、昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する有機金属化合物を用いた表面層改質によって、表面層がX線および/または電子線および/または放射線吸収機能を付与されたことを特徴とする。

【0063】上記目的を達成するために、また、本願の請求項43記載の発明に係る樹脂成形物は、請求項1、請求項2、請求項3、請求項4、請求項5、請求項6、請求項7、請求項8、請求項9、請求項10、請求項11、または、請求項12に記載の樹脂表面層の改質方法、および、昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する抗菌防カビ剤を用いた表面層改質によって、表面層が抗菌防カビ機能を付与されたことを特徴とする。

【0064】上記目的を達成するために、また、本願の請求項44記載の発明に係る樹脂成形物は、請求項1、請求項2、請求項3、請求項4、請求項5、請求項6、請求項7、請求項8、請求項9、請求項10、請求項11、または、請求項12に記載の樹脂表面層の改質方法、および、昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する薬理活性有機化合物を用いた表面層改質によって、表面層が薬理活性機能を付与されたことを特徴とする。



【0065】上記目的を達成するために、また、本願の請求項45記載の発明に係る樹脂成形物は、請求項1、請求項2、請求項3、請求項4、請求項5、請求項6、請求項7、請求項8、請求項9、請求項10、請求項11、または、請求項12に記載の樹脂表面層の改質方法、および、昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有し、動植物に対して生理活性を示す有機化合物を用いた表面層改質によって、表面層が農薬としての機能を付与されたことを特徴とする。

【0066】

【発明の実施の形態】以下、本発明の好適な実施の形態について、詳説する。

【0067】〔樹脂表面層の改質〕本発明において樹脂成形物表面層の改質とは、樹脂成形物の表面から所定の深さまでの表面層部分の物性、例えば、密度、硬度、衝撃強度、弾性率、音速、誘電率、透磁率、電気伝導度、表面抵抗、体積抵抗、光導電性、静電気帯電順位、帯電性、光透過率、光反射率、偏光性、屈折率、2次光非線形感受率、3次光非線形感受率、非線形屈折率、親水性、水との接触角、疎水性、親油性、ガス透過率、吸水率、などを樹脂単独の場合とは変えることを言う。また、樹脂成形物表面層を改質することによって、樹脂単独の場合に比べ、酸化分解反応、熱分解反応、紫外線および/または可視光線による光分解反応などが抑制される場合を含める。また、樹脂成形物表面層を改質することによって、樹脂単独の場合に比べ、蛍光、燐光、フォトリソミック、フォトリフラクティブ効果、などの機能を樹脂成形物表面層に付与する場合を含める。更に、樹脂成形物表面層を改質することによって、抗菌作用、防カビ作用などの生理活性機能および/または薬理活性機能を樹脂成形物表面層に付与する場合を含める。

【0068】ここで、改質される表面層の厚さ、すなわち、表面からの深さは、原子または分子1個のレベルを下限として、樹脂成形物全体が改質される場合を上限とする。

【0069】〔樹脂表面層の着色〕樹脂成形物表面層が改質されたことによって、表面層の光透過率および/または光反射率および/または屈折率が変わると、改質前とは外見上の色が変わる。すなわち、樹脂表面層の着色は、表面改質の1種であることと見なすことができる。樹脂表面層の物性を変えるために用いた昇華性有機化合物が有色であれば、樹脂表面層の色は、樹脂本来の色に有色有機化合物を加えた色となる。

【0070】本発明では、樹脂成形物の外見上の色を変えることを目的として樹脂表面層を改質することを「着色」と呼ぶものとする。

【0071】〔樹脂成形物〕本発明の樹脂成形物表面層の改質・着色方法は、昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する有機化合物を、前記有機化合物の飽和昇華圧状態に置き、前記有機化合物蒸気を

前記樹脂成形物表面に均一に付着させ、付着した前記有機化合物を前記樹脂成形物表面から内部に浸透・分散させることを特徴とするものである。

【0072】ここで、樹脂成形物は、任意の形態であってよい。具体的には、樹脂素材をブロック状、球状、半球状、ペレット状、円柱状、パイプ状、チューブ状、直方体、立方体、プリズム状、円錐、三角錐、四角錐、レンズ状、平板状、シート状、フィルム状、薄膜状、ガラス等の基板上に設けられた薄膜状、ファイバー状、繊維、プラスチック光ファイバーなどの形態に成形したもの、または射出成形法などの成形方法によって任意の形状を付与されたプラスチック成形物、などを用いることができる。繊維状の樹脂成形物は、更に加工されて、紡糸された糸状、織物状、不織布状などの形態を取っていても良い。

【0073】また、樹脂成形物の大きさについて特に制限はない。すなわち、粒子の外寸が数百マイクロメートルから数ナノメートルの樹脂の粉末および/または微粉末であってもよい。

【0074】また、2種類以上の樹脂を組み合わせで成形したものであってもよい。例えば、昇華性有機化合物と親和性のある樹脂を表面第1層にして、この第1層の下に他の2種類以上の樹脂を積層構造にしたシート状の構造の樹脂成形物を用いることができる。更に、樹脂以外の材質からなる構造体の表面を昇華性有機化合物と親和性のある樹脂の膜で覆ったものであってもよい。例えば、ガラスレンズまたはプラスチックレンズの表面に昇華性有機化合物と親和性のある樹脂の薄膜をコートしたものをを用いることもできる。

【0075】〔樹脂〕本発明において「樹脂」とは、有機化合物の重合体、有機高分子化合物、プラスチック、ポリマー、オリゴマーを含む。熱可塑性であっても、熱硬化性であってもよい。その具体例としては、ケトン樹脂、ノルボルネン樹脂、ポリスチレン、ポリ(α-メチルスチレン)、ポリインデン、ポリ(4-メチル-1-ペンテン)、ポリビニルピリジン、ポリアセタール、ポリビニルホルマール、ポリビニルアセタール、ポリビニルブチラール、ポリ酢酸ビニル、ポリプロピオン酸ビニル、ポリビニルアルコール、ポリエチレン、ポリプロピレン、ポリブタジエン、ポリメチルペンテン、ポリ塩化ビニル、塩素化ポリ塩化ビニル、塩素化ポリエチレン、塩素化ポリプロピレン、ポリ塩化ビニリデン、ポリテトラフルオロエチレン、ポリクロロトリフルオロエチレン、ポリフッ化ビニリデン、ポリビニルメチルエーテル、ポリビニルエチルエーテル、ポリビニルベンジルエーテル、ポリビニルメチルケトン、ポリ(N-ビニルカルバゾール)、ポリ(N-ビニルピロリドン)、ポリアクリル酸メチル、ポリアクリル酸エチル、ポリアクリル酸、ポリアクリロニトリル、ポリメタクリル酸メチル、ポリメタクリル酸エチル、ポリメタクリル酸ブチ

ル、ポリメタクリル酸ベンジル、ポリメタクリル酸シクロヘキシル、ポリメタクリル酸、ポリメタクリル酸アミド、ポリメタクリロニトリル、ポリアセトアルデヒド、ポリクロラール、ポリエチレンオキシド、ポリプロピレンオキシド、ポリエチレンテレフタレート、ポリブチレンテレフタレート、ポリカーボネート類（ビスフェノール類+炭酸）、ポリサルホン、ポリエーテルサルホン、ポリフェニレンサルファイド、ポリ（ジエチレングリコール・ビスアリルカーボネート）類、6-ナイロン、6, 6-ナイロン、12-ナイロン、6, 12-ナイロン、ポリアスパラギン酸エチル、ポリグルタミン酸エチル、ポリリジン、ポリプロリン、ポリ（γ-ベンジルーレーグルタメート）、メチルセルロース、エチルセルロース、ベンジルセルロース、ヒドロキシエチルセルロース、ヒドロキシプロピルセルロース、アセチルセルロース、セルローストリアセート、セルローストリブチレート、アルキド樹脂（無水フタル酸+グリセリン）、脂肪酸変性アルキド樹脂（脂肪酸+無水フタル酸+グリセリン）、不飽和ポリエステル樹脂（無水マレイン酸+無水フタル酸+プロピレングリコール）、エポキシ樹脂（ビスフェノール類+エピクロルヒドリン）、エポキシ樹脂（クレゾールノボラック+エピクロルヒドリン）、ポリウレタン樹脂、フェノール樹脂、尿素樹脂、メラミン樹脂、キシレン樹脂、トルエン樹脂、フラン樹脂、グアナミン樹脂、ジアリルフタレート樹脂などの樹脂、ポリ（フェニルメチルシラン）などの有機ポリシラン、有機ポリゲルマンおよびこれらの共重合・共重縮合体が挙げられる。コポリマーとしては、アクリロニトリル+スチレン（AS樹脂）、アクリロニトリル+アクリレート+スチレン（AAS樹脂）、アクリロニトリル+エチレン+スチレン（AES樹脂）、アクリロニトリル+ブタジエン+スチレン（ABS樹脂）、アクリロニトリル+塩素化ポリエチレン+スチレン（ACS樹脂）、メチルメタクリレート+ブタジエン+スチレン（MBS樹脂）、エチレン-塩化ビニルコポリマー、エチレン-酢酸ビニルコポリマー、エチレンビニルアルコールコポリマーなどのプラスチックを挙げることができる。また、二硫化炭素、四フッ化炭素、エチルベンゼン、パーフルオロベンゼン、パーフルオロシクロヘキサンまたはトリメチルクロロシラン等、通常では重合性のない化合物をプラズマ重合して得た高分子化合物などを使用することができる。

【0076】〔昇華性有機化合物〕昇華とは固体が中間相である液体を経由せずに直接気体に変化する過程であり、三重点の温度以下であればすべての固体について起こる普遍的現象である。しかしながら、例えば、大分子量のアゾ化合物、ポリメチン色素などのイオン性結晶、などの有機化合物は常温以上に加熱していった場合、圧力によらず、融点を示さずに熱分解してしまう。このような物質には三重点は事実上存在せず、昇華することは

ない、と行うことができる。このような物質と区別するため、熱分解を伴わずに昇華可能な有機化合物を「昇華性有機化合物」と呼ぶこととする。

【0077】昇華性有機化合物の具体例として、例えば、以下のような化合物群を挙げることができる。

【0078】昇華性かつ無色の有機化合物として、2, 6-ジ-tert-ブチル-p-クレゾール、ブチル化ヒドロキシアニソール、2, 6-ジ-tert-ブチル-4-エチルフェノール、2, 2'-メチレンビス（4-メチル-6-tert-ブチルフェノール）、2, 2'-メチレンビス（4-エチル-6-tert-ブチルフェノール）、などのフェノール誘導体を用いることができる。これらの化合物はプラスチックの酸化防止剤として知られており、これらを用いて樹脂表面層を改質することによって、表面層の酸化防止作用を強化することができる。また、樹脂成形物の色を変えずに、樹脂表面層の密度、硬度、衝撃強度、弾性率、音速、誘電率、静電気帯電順位、帯電性、屈折率などを変える目的にも用いることができる。

【0079】昇華性かつ無色ないし淡黄色の有機化合物として、サリチル酸フェニル、サリチル酸p-tert-ブチルフェニル、サリチル酸p-オクチルフェニル、2, 4-ジヒドロキシベンゾフェノン、2-ヒドロキシ-4-メトキシベンゾフェノン、2, 2'-ジヒドロキシ-4-メトキシベンゾフェノン、2, 2'-ジヒドロキシ-4, 4'-ジメトキシベンゾフェノン、2-（2'-ヒドロキシ-5'-メチルフェニル）ベンゾトリアゾール、2-（2'-ヒドロキシ-5'-tert-ブチルフェニル）ベンゾトリアゾール、2-（2'-ヒドロキシ-3', 5'-ジ-tert-ブチルフェニル）ベンゾトリアゾール、2-（2'-ヒドロキシ-3'-tert-ブチル-5-メチルフェニル）-5-クロロベンゾトリアゾール、2-（2'-ヒドロキシ-3', 5'-ジ-tert-ブチルフェニル）-5-クロロベンゾトリアゾール、2-〔（2'-ヒドロキシ-3'-（3'', 4'', 5'', 6''-テトラヒドロフタライミドメチル）-5'-メチルフェニル）ベンゾトリアゾール、2-（2'-ヒドロキシ-5'-メタアクリロキシフェニル）-2H-ベンゾトリアゾール、エチル-2-シアノ-3, 3'-ジフェニルアクリレート、などを挙げることができる。これらの化合物はプラスチック用の紫外線吸収剤として知られており、これらを用いて樹脂表面層を改質することによって、表面層の紫外線吸収作用を強化することができる。また、樹脂成形物の色を変えずに、樹脂表面層の密度、硬度、衝撃強度、弾性率、音速、誘電率、静電気帯電順位、帯電性、屈折率などを変える目的にも用いることができる。

【0080】2次非線形光学効果を示す単結晶を形成する有機分子化合物であって、昇華性の有機化合物として、尿素およびその誘導体、m-ニトロアニリン、2-

メチル-4-ニトロアニリン、2-(N,N-ジメチルアミノ)-5-ニトロアセトアニリド、N,N'-ビス(4-ニトロフェニル)メタンジアミンなどのベンゼン誘導体、4-メトキシ-4'-ニトロビフェニルなどのビフェニル誘導体、4-メトキシ-4'-ニトロスチルベンなどのスチルベン誘導体、4-ニトロ-3-ピコリン=N-オキシドなどのピリジン誘導体、2',4,4'-トリメトキシカルコンなどのカルコン誘導体、チエニルカルコン誘導体などを挙げることができる。これらの有機化合物は無色ないし黄色であるため、樹脂表面層本来の色を変えずに、樹脂表面層の密度、硬度、衝撃強度、弾性率、音速、誘電率、静電気帯電順位、帯電性、屈折率、3次光非線形感受率、非線形屈折率、フォトリフラクティブ効果特性、などを変えるために用いることができる。

【0081】紫外～可視光線～近赤外線の波長帯域において光吸収を示し、昇華性の有機化合物(有機色素)の具体例として、アゾ色素、ポルフィリン色素、フタロシアニン色素、トリフェニルメタン系色素、ナフトキノ色素、アントラキノ色素、ナフタレンテトラカルボン酸ジイミド色素、ペリレンテトラカルボン酸ジイミド色素などを挙げることができる。これらの色素を用いることで、樹脂成形物表面樹脂層の着色を行うことができる。また、これらの色素が蛍光を呈する場合、樹脂成形物の表面層に蛍光を呈する機能を付与することができる。

【0082】昇華性アゾ色素の具体例としては、例えば、アゾベンゼン、4-ジメチルアミノアゾベンゼン、4-ジメチルアミノ-3'-ニトロアゾベンゼン、4-ジメチルアミノ-4'-ニトロアゾベンゼン、4-ジメチルアミノ-3-メチル-3'-ニトロアゾベンゼン、4-ジメチルアミノ-3-メチル-4'-ニトロアゾベンゼン、4-ニトロアゾベンゼンなどを挙げることができる。

【0083】ポルフィリン色素の具体例としては、例えば、ポルフィリン、テトラフェニルポルフィリンなどを挙げることができる。

【0084】フタロシアニン色素の具体例としては、例えば、フタロシアニン、銅フタロシアニン、コバルトフタロシアニン、ニッケルフタロシアニン、クロロアルミニウムフタロシアニンなどを挙げることができる。

【0085】トリフェニルメタン系色素の具体例としては、例えば、クリスタルバイオレットラクトン、3-ジエチルアミノ-6-メチル-7-クロロフルオラン、3-ジエチルアミノ-7-メチルアミノフルオラン、3-ジエチルアミノ-7-フェニルアミノフルオランなどを挙げることができる。

【0086】ナフトキノ色素の具体例としては、例えば、1,4-ナフトキノ、2,3-ジクロロ-1,4-ナフトキノ、5-アミノ-2,3-ジクロロ-1,

4-ナフトキノ、8-フェニルアミノ-5-アミノ-2,3-ジシアノ-1,4-ナフトキノなどを挙げることができる。

【0087】アントラキノ色素の具体例としては、例えば、アントラキノ、1-アミノアントラキノ、1,4-ジヒドロキシアントラキノなどを挙げることができる。

【0088】ナフタレンテトラカルボン酸ジイミド色素の具体例としては、例えば、1,4,5,8-ナフタレンテトラカルボン酸ジイミド、N,N'-ジメチル-1,4,5,8-ナフタレンテトラカルボン酸ジイミドなどを挙げることができる。

【0089】ペリレンテトラカルボン酸ジイミド色素の具体例としては、例えば、3,4,9,10-ペリレンテトラカルボン酸ジイミド、N,N'-ジ-tert-ブチル-3,4,9,10-ペリレンテトラカルボン酸ジイミドなどを挙げることができる。

【0090】フォトクロミック現象を起こし、昇華性かつ結晶性の有機化合物として、6-プロモ-1',3'-ジヒドロ-1',3',3'-トリメチル-8-ニトロスピロ[2H-1-ベンゾピラン-2,2'-(2H)-インドール]、5-クロロ-1,3-ジヒドロ-1,3,3-トリメチルスピロ[2H-インドール-2,3'-[3H]ナフト[2,1-b][1,4]オキサジン]、5-クロロ-1,3-ジヒドロ-1,3,3-トリメチルスピロ[2H-インドール-2,3'-[3H]ナフト[9,10-b][1,4]オキサジン]、6,8-ジプロモ-1',3'-ジヒドロ-1',3',3'-トリメチルスピロ[2H-1-ベンゾピラン-2,2'-(2H)-インドール]、1',3'-ジヒドロ-1',3',3'-トリメチル-6-ニトロスピロ[2H-1-ベンゾピラン-2,2'-(2H)-インドール]、1',3'-ジヒドロ-5'-メトキシ-1',3',3'-トリメチル-6-ニトロスピロ[2H-1-ベンゾピラン-2,2'-(2H)-インドール]、1',3'-ジヒドロ-8-メトキシ-1',3',3'-トリメチル-6-ニトロスピロ[2H-1-ベンゾピラン-2,2'-(2H)-インドール]、1,3-ジヒドロ-1,3,3-トリメチルスピロ[2H-インドール-2,3'-[3H]ナフト[2,1-b][1,4]オキサジン]、1,3-ジヒドロ-1,3,3-トリメチルスピロ[2H-インドール-2,3'-[3H]フェナンスロ[9,10-b][1,4]オキサジン]、1,3-ジヒドロ-1,3,3-トリメチルスピロ[2H-インドール-2,3'-[3H]ナフト[2,1-b]ピラン]、1,3-ジヒドロ-5-メトキシ-1,3,3-トリメチルスピロ[2H-インドール-2,3'-[3H]ナフト[2,1-b]ピラン]などのスピロピラン類; 2,5-ジメチル-3-フリルエチリデンコハク酸無水物、

2, 5-ジメチル-3-フリリイロプロピリデンコハク酸無水物などのフルギド類; 2, 3-ビス(2, 4, 5-トリメチル-3-チエニル)マレイン酸無水物、2, 3-ビス(2, 4, 5-トリメチル-3-チエニル)マレイミド、*cis*-1, 2-ジシアノー-1, 2-ビス(2, 4, 5-トリメチル-3-チエニル)エテンなどのジアリールエテン類などを挙げることができる。これらのフォトクロミック色素を用いて樹脂表面層を改質することによって、樹脂成形物の表面層にフォトクロミック特性を付与することができる。

【0091】昇華性の有機金属化合物として、チタノセン、バナジノセン、クロモセン、マンガノセン、フェロセン、コバルトセン、ニッケロセン、ルテノセンなどのメタルセンを挙げることができる。これら昇華性の有機金属化合物を用いて樹脂表面層を改質することによって、X線や電子線の透過率特性を変えることができる。

【0092】また、バナジノセン、クロモセン、マンガノセン、コバルトセン、ニッケロセン、などは磁気モーメントがあるので、これら昇華性の有機金属化合物を用いて樹脂表面層を改質することによって、磁気的性質を変えることができる。

【0093】昇華性の有機化合物として、ジクロロフェノール類、トリクロロフェノール類、テトラクロロフェノール類、ペンタクロロフェノール類、p-クロロ-m-キシレノール、p-クロロ-m-クレゾール、4-クロロ-2-フェニルフェノール、2, 4, 5, 6-テトラクロロイソフタロニトリル、10, 10'-オキシビスフェノキシアルシン、N-(トリクロロメチルチオ)フタルイミド、N-(フルオロジクロロメチルチオ)フタルイミドなどを挙げることができる。これらの化合物はプラスチック用の防腐・防カビ剤として知られており、これらを用いて樹脂表面層を改質することによって、樹脂表面層に抗菌防カビ機能を付与することができる。本発明の樹脂成形物表面層の改質方法を用いることによって、プラスチック全体に防腐・防カビ剤を練り込む場合に比べ、防腐・防カビ剤の使用量を必要最小限に留めることが可能になる。

【0094】同様にして、昇華性の有機化合物として、薬理活性のある有機化合物を用いて樹脂表面層を改質することによって、樹脂表面層に医薬および/または農薬としての機能を付与することができる。例えば、レーメントール(融点43℃)を用いることで鎮痛作用を、また、樟脳(融点179℃)を用いることで強心作用を、樹脂成形物、例えばプラスチックフィルムの表面層の機能として付与することができる。同様にして、例えばプラスチックシートの表面層に、例えば、除草機能、殺虫機能、害虫禁避機能、植物成長促進機能、植物成長抑制剤などの農薬機能を付与することができる。

【0095】昇華性かつ結晶性の有機化合物として、3, 4-ジメトキシベンズアルデヒド(融点40℃)、

3-オキシ-2-メチル-4-ピロン(融点161℃)などを挙げることができる。これらの化合物は香料としてももちいられており、これらを用いて樹脂表面層を改質することによって、樹脂表面層に強い香りを発生する機能を付与することができる。

【0096】

【実施例】以下、実施例を示し、更に詳しくこの発明の方法について説明する。

【0097】【実施例1】図1に示すように、一端を閉じたガラス管10(例えば、外径15mm、内径12mm、長さ200mm)内に、昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する有機化合物20として*cis*-1, 2-ジシアノー-1, 2-ビス(2, 4, 5-トリメチル-3-チエニル)エテン(融点121℃; 東京化成工業製)の結晶5mgと、樹脂成形物としてビスフェノールAポリカーボネート(アルドリッチケミカル株式会社製)のペレット(外径約2.5mm、長さ2.5mmの円柱状)5~6個を設置した。その後、図2(A)に示すように、ガラス管10の他端を真空排気装置50に接続して室温下において管内の圧力が $10^{-5}$ Pa以下になるまで排気を行った。次いで、図2(B)に示すように、前記ガラス管10の接続端に近い部分をガラス管封管用バーナー60にて熔融封管して、前記有機化合物および前記樹脂ペレットを両端を封じたガラス封管11内に密閉した。

【0098】次に、図3に示すように、前記ガラス封管11を恒温槽70内に設置し、前記ガラス封管11全体にわたって、前記昇華性有機化合物が熱分解せずに昇華する温度(上記化合物の場合、110℃)を下限とし、次の条件を満たす温度の内、最も高い温度を上限として、精密に温度制御しながら加熱した。

【0099】(a)前記昇華性有機化合物の熔融開始温度を越えない温度、(b)前記樹脂のガラス転移温度(ポリカーボネートの場合、約150℃)、(c)前記樹脂の熱変形開始温度、(d)前記樹脂の熔融開始温度、(e)前記樹脂の分解開始温度を越えない温度。

【0100】なお、樹脂成形物の表面平滑性や表面における微細構造を失うことなく、本発明の樹脂表面層改質および/または着色方法を実施する場合は、前記樹脂の熱変形開始温度を越えないよう、温度制御する必要がある。

【0101】本実施例では、恒温槽70の内部温度を110℃に設定し、設定温度に対して $\pm 0.1^\circ\text{C}$ の精度で24時間維持した。その後、恒温槽70の温度を25℃まで9時間かけて徐々に低下させた。なお、ここで、例えば前記ガラス封管11を恒温槽外に取り出すなどして急速に冷却すると、前記昇華性有機化合物の蒸気が、冷却された前記ガラス封管11の内壁に触れて凝集し、結晶として析出してしまい、樹脂表面層内に昇華性有機化合物が所定量均一に浸透・分散されないおそれがある。

【0102】本実施例では、徐々に室温まで冷却し、冷却前記ガラス封管11を取り出し、ガラス封管11を切断して、表面層に前記昇華性有機化合物が浸透・分散したポリカーボネートのペレットを取り出した。このペレットをカッターで輪切りにして光学顕微鏡で観察し、図10に示すような断面写真を撮影した。図10中に挿入したスケールの1目盛は10マイクロメートルである。図10から明らかなようにポリカーボネートのペレットの表面から約90マイクロメートルの深さにわたって、表面層に前記昇華性有機化合物が浸透・分散して、表面層が改質・着色されたことが判る。

【0103】更に、得られた樹脂表面層の光吸収スペクトルの測定、光学顕微鏡観察（通常視野）、偏光顕微鏡観察、前記樹脂ペレット表面の走査型電子顕微鏡観察、および、前記樹脂ペレット断面の透過型電子顕微鏡観察によって、前記樹脂ペレットの内部に、前記昇華性有機化合物が分子分散すなわち固溶化し、表面層が改質・着色されていることが確認された。なお、得られた樹脂ペレットの表面および内部に、前記昇華性有機化合物の結晶は観察されなかった。

【0104】前記昇華性有機化合物、cis-1, 2-ジシアノ-1, 2-ビス(2, 4, 5-トリメチル-3-チエニル)エテンの浸透によって改質・着色されたポリカーボネート表面層は、紫外線をカットした可視光線および/または赤外線の照射で黄色に、紫外線の照射によって赤色に変化することが観察された。すなわち、樹脂表面層がフォトクロミック機能を付与されたことが確認された。

【0105】図3は本発明の樹脂表面層改質および/または着色装置の最も単純な実施形態を示すものである。すなわち、両端を封じたガラス管11内には、樹脂成形物（樹脂ペレット30）と、前記樹脂成形物の樹脂と親和性がありかつ昇華性を有する有機化合物20とが配置されている。このガラス管11内で、前記有機化合物は飽和昇華圧状態に置かれる。また、恒温槽70は、前記有機化合物が昇華し、前記有機化合物の蒸気が前記樹脂成形物表面に付着し、更に前記有機化合物を前記樹脂成形物中に浸透・分散させるための加熱手段である。

【0106】【比較例1】一端を閉じたガラス管10（例えば、外径15mm、内径12mm、長さ200mm）内に、昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する有機化合物20として例えば、cis-1, 2-ジシアノ-1, 2-ビス(2, 4, 5-トリメチル-3-チエニル)エテンの結晶のみを入れた以外は、実施例1と同様に、ガラス封管11の加熱および徐冷を行った。加熱時に昇華して発生した前記昇華性有機化合物の蒸気は、徐冷の際、元の結晶の表面に戻り、ガラス管11のガラス壁に付着することはなかった。なお、加熱状態にあるガラス封管11を恒温槽から取り出して急速に冷却すると、前記昇華性有機化合物の

蒸気が、冷却された前記ガラス封管11の内壁に触れて凝集し、結晶として析出し、前記ガラス封管11の内壁に付着した。このように、急冷したとき、ガラス封管内壁へ結晶が析出することから、加熱によって昇華が進行し、ガラス封管内に前記昇華性有機化合物の蒸気が充満していることが判る。

【0107】【実施例2】ポリメタクリル酸メチル(PMMA):2.0gをアセトン:200mlに溶解した。この溶液を、n-ヘキサン:800ml中へかき混ぜながら加えて、析出した樹脂粉末を濾別した。この樹脂粉末をn-ヘキサンで洗浄した後減圧下で乾燥させ、次いで粉碎した。得られた樹脂粉末を $10^{-5}$ Pa未満の超高真空中、100℃で2日間加熱を続け、残留溶媒等の揮発成分を完全に除去した。この粉末100mgを、ガラス基板（厚さ0.14mm、幅10mm、長さ20mm）とアルミホイル（厚さ20μm、幅10mm、長さ20mm）との間に厚さ100μmのスペーサーとともに挟み、更にアルミホイルの上にもう1枚のガラス板を重ね、真空中150℃に加熱し、2枚のガラス板を圧着する方法（真空ホットプレス法）を用いてガラス基板/アルミホイル間にPMMAの膜（膜厚約100μm）を作製した。次いで、充分冷却した後、アルミホイルを剥がして、ガラス基板40上に成膜されたPMM A薄膜33を得た。

【0108】一端を閉じたガラス管10（例えば、外径15mm、内径12mm、長さ200mm）内に、昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する有機化合物20として、cis-1, 2-ジシアノ-1, 2-ビス(2, 4, 5-トリメチル-3-チエニル)エテンの結晶20mgと、前記樹脂薄膜33が形成されたガラス基板とを設置し、ガラス管10の他端を真空排気装置50に接続して室温下において管内の圧力が $10^{-5}$ Pa以下になるまで排気を行った。その後、前記ガラス管10の接続端に近い部分をガラス管封管用バーナー60にて熔融封管して、両端を封じたガラス封管11内に前記有機化合物と前記樹脂薄膜を密閉した。

【0109】図4に示すように、前記ガラス封管11を恒温槽70内に設置し、前記ガラス封管11全体にわたって、前記昇華性有機化合物が熱分解せずに昇華する温度（上記化合物の場合、110℃）において、精密に温度制御しながら加熱した。5時間後、恒温槽70の温度を25℃まで9時間かけて徐々に低下させた。

【0110】得られた樹脂薄膜の光吸収スペクトルの測定、光学顕微鏡観察（通常視野）、偏光顕微鏡観察、前記樹脂薄膜表面の走査型電子顕微鏡観察、および、前記樹脂薄膜断面の透過型電子顕微鏡観察によって、前記樹脂薄膜33の表面層に、深さ約20マイクロメートルにわたり前記昇華性有機化合物が分子分散すなわち固溶化していることが確認された。なお、得られた樹脂薄膜の表面および内部に、前記昇華性有機化合物の結晶は観察

されなかった。すなわち、ガラス基板40上に成膜されたPMMA樹脂薄膜33の表面から前記昇華性有機化合物が浸透・分散して、表面層（厚さ20 $\mu$ m）が改質・着色されたことが判る。

【0111】本実施例で作製したcis-1, 2-ジシアノ-1, 2-ビス（2, 4, 5-トリメチル-3-チエニル）エテンによって改質されたポリカーボネート樹脂薄膜は、紫外線をカットした可視光線および／または赤外線の照射で黄色に、紫外線の照射によって赤色に変化する。すなわち、フォトクロミック薄膜として機能することが確認された。400nm未満の波長の光をカットした可視光線および赤外線を20分照射して、黄色になったものに、ブラックライトの紫外線（中心波長366nm）を2, 4, 6, 8, 10時間照射して吸収スペクトルの変化を測定した結果を図11に示す。波長400nm以上の可視光線および赤外線照射20分後のスペクトルを点線、紫外線照射2時間後を長い鎖線、同4時間後を短い鎖線、同6時間後を2点鎖線、同8時間後を1点鎖線、同10時間後を実線で示す。

【0112】〔実施例3〕実施例2におけるPMMA基板の他に、ポリ（メタクリル酸2-ヒドロキシプロピル）（PHPMA）を真空ホットプレス法によりガラス基板40（例えば、厚み0.14mm、幅10mm、長さ50mm）上に形成した樹脂薄膜33（膜厚100 $\mu$ m）を有するガラス基板40を作製した。そして、この異なる種類の樹脂薄膜が各々形成された2枚のガラス基板40を同一のガラス封管11に入れ、昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する有機化合物20とともに実施例2と同様にして加熱および徐冷を行った。スペクトル観察の結果、PMMA薄膜には実施例2と同様に前記昇華性有機化合物が固溶化し、表面層が改質・着色されていることが確認された。一方、得られたPHPMA薄膜の紫外・可視・赤外線吸収スペクトルには、前記昇華性有機化合物に帰属される吸収は確認されなかった。この結果は、前記昇華性有機化合物はPMMAには親和性があるが、PHPMAには全く親和性がない、また、親和性がない場合、樹脂薄膜中への浸透・分散は起こらない、と解釈することができる。

【0113】〔比較例2〕真空ホットプレス法によりガラス基板40（例えば、厚み0.14mm、幅10mm、長さ50mm）上にポリ（メタクリル酸2-ヒドロキシプロピル）（PHPMA）を成形した樹脂薄膜33（膜厚100 $\mu$ m）のみを入れたガラス封管11について、昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する有機化合物20とともに実施例2と同様にして加熱および徐冷を行った。スペクトル観察の結果、得られたPHPMA薄膜の吸収スペクトルには、前記昇華性有機化合物に帰属される吸収は確認されなかった。

【0114】以上、実施例1, 2および3、比較例1および2の観察から、減圧されたガラス封管内において加

熱時、前記昇華性有機化合物が昇華し、ガラス管内に蒸気が充満すること、その蒸気を冷却すると蒸着過程が進行すること、冷却せずに加熱状態を保ち、そこに前記昇華性有機化合物と親和性のある樹脂成形物（ペレットや樹脂薄膜）を置くと、樹脂表面層中に前記昇華性有機化合物が分子分散・固溶化して表面層が改質および／または着色されることが確認された。一方、前記昇華性有機化合物と親和性のある樹脂成形物が存在しない場合、一旦前記昇華性有機化合物は昇華するものの、徐冷によって、前記昇華性有機化合物蒸気は結晶表面に戻ること、が確認された。

【0115】ここで、前記昇華性有機化合物と樹脂の親和性に関しては「溶媒とエネルギーによる安定化の有無」として理解することができる。すなわち、樹脂は、ここでは前記昇華性有機化合物に対する「媒質」、溶液の場合の「溶媒」として作用している。前記昇華性有機化合物と樹脂の親和性が認められないケースでは、樹脂は「溶解度ゼロの媒質」として作用している。この場合、「溶媒とエネルギーによる安定化はなし」であるから、前記昇華性有機化合物蒸気が樹脂中に浸透・分散することはあり得ない。従って、飽和蒸気圧状態まで加熱した後、徐冷していくと、前記昇華性有機化合物の蒸気は再度結晶表面に戻って結晶化するのが熱力学的に最も安定である。一方、「溶媒とエネルギーによる安定化がある」場合、樹脂表面に到達した前記昇華性有機化合物蒸気は、再び気化し、結晶表面に戻るよりも、樹脂中へ固溶化の方が安定化する。換言すると、「溶媒とエネルギーによる安定化がある」場合、真空を媒介として、結晶表面から樹脂中への「溶解」が進行していく。なお、「親和性の有無」に関しては、再結晶精製に適した溶媒を探索する場合と同様に、分子部分構造の類似性や溶解性パラメーターなどの経験則に基づき、試行錯誤的に探索する必要がある。その際、計算化学の手法を活用することも可能である。

【0116】〔実施例4〕一端を閉じたガラス管10（外径15mm、内径12mm、長さ200mm）を3本用意し、各々の中に、昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する有機化合物20として、cis-1, 2-ジシアノ-1, 2-ビス（2, 4, 5-トリメチル-3-チエニル）エテンの結晶20mgと、樹脂成形物として、ビスフェノールAポリカーボネート（アルドリッチケミカル株式会社製）のペレット30（外径約2.5mm、長さ2.5mmの円柱状）5～6個を設置し、ガラス管10の他端を真空排気装置50に接続して室温下において管内の圧力が10～5Pa以下になるまで排気を行った。その後、前記ガラス管の接続端に近い部分をガラス管封管用バーナー60にて溶融封管して、両端を封じたガラス封管11内に前記有機化合物および前記樹脂成形物を密閉した。

【0117】3本の前記ガラス封管11を1本ずつ恒温

槽70内に設置し、前記ガラス封管11全体にわたって、前記昇華性有機化合物が熱分解せずに昇華する温度（上記化合物の場合、110℃）において、精密に温度制御しながら加熱した。加熱時間は、3本について各々12時間、24時間、48時間とした。加熱終了後、恒温槽70の温度を25℃まで9時間かけて徐々に低下させた。いずれの場合も、前記昇華性有機化合物の結晶は残留していた。

【0118】加熱処理時間を12、24および48時間とした3種の前記樹脂ペレット各々について、断面の光学顕微鏡観察を行ったところ、前記昇華性有機化合物が浸透・固溶化した深さは、加熱処理時間に応じてそれぞれペレット表面から55μm、100μm、190μmであった。すなわち、昇華性有機化合物が十分に存在する場合、加熱処理時間によって、前記昇華性有機化合物の浸透・固溶化する深さ、すなわち改質させる表面層の厚さを制御できることが判った。なお、言うまでもなく、昇華性有機化合物の樹脂成形物に対する仕込量を制御することによっても、改質させる表面層の厚さを制御することができる。

【0119】〔実施例5〕図5は、本実施例の樹脂表面層改質および/または着色装置の概略構成を示す断面図である。

【0120】樹脂成形物としては、円形ガラス基板400（例えば、直径120mm、厚さ0.6mm）の1面にスピコート法によってポリカーボネート樹脂のジクロロメタン溶液を塗工し、10-5Paの高真空中、150℃で2時間脱気処理した樹脂膜300（膜厚1μm）を用いた。

【0121】一方、昇華性有機化合物（例えば、cis-1,2-ジシアノ-1,2-ビス（2,4,5-トリメチル-3-チエニル）エテン）を溶融法により昇華源基板240（アルミニウム板、例えば、直径120mm、厚さ2mm）上に成膜し、昇華源を作製した。

【0122】そして、上記樹脂膜300に対峙するように、上記昇華源を設置した。樹脂膜300と成膜された昇華性有機化合物200との面間隔は、例えば、5mmとした。この面間隔が短い程、昇華源から発生した昇華性有機化合物の蒸気は、短時間で樹脂膜表面に到達する。しかしながら、この間隔を極端に短くすると、密閉式容器内部を減圧にする際、排気抵抗が増してしまう。1mmないし10mm程度が好ましい。

【0123】密閉式容器外壁110はステンレスまたはアルミニウムからなり、基板の出し入れのため、上下に分割可能な構造（図示せず）とする。

【0124】密閉式容器内部100は真空弁190および真空配管系120を経由して真空排気系150に接続されており、室温下において密閉式容器内部100の圧力が10-5Pa以下になるまで排気を行った後、弁190を閉じる。これにより、密閉式容器は密閉される。

【0125】加熱手段として用いられるヒーター710、昇華源基板ヒーター720、樹脂膜ガラス基板ヒーター740、および、真空弁ヒーター790は、例えば、真空仕様のシーズ電気発熱線を埋め込んだアルミニウムからなるものを用いることができる。伝熱性の高い材質からなるヒーターを隙間なく設置することによって、密閉式容器内部100および真空弁190の部分を均一に加熱することができる。ここで、仮に、密閉式容器内部100および/または真空弁190の一部分に、他よりも温度の低い箇所が存在する場合、昇華によって発生した昇華性有機化合物の蒸気が、その部分で冷却され、結晶化・堆積するおそれがあるので注意が必要である。

【0126】昇華源基板240と昇華源基板ヒーター720、および、円形ガラス基板400と樹脂膜ガラス基板ヒーター740は、それぞれ複数の保持爪（図示せず）によって、基板とヒーターとが密着させられているものとする。

【0127】本実施例の場合、密閉式容器内部100を減圧にしてから、上記加熱手段により、加熱を行い、全体が設定温度（例えば、110℃）±1℃になるよう、精密に温度制御を行った。

【0128】24時間、加熱を止め、密閉式容器内部の温度を25℃まで12時間かけて徐々に低下させた。次いで、密閉式容器内部を大気圧に戻し、円形ガラス基板400上の樹脂膜300を取り出した。

【0129】得られた樹脂膜300の光吸収スペクトルの測定、光学顕微鏡観察（通常視野）、偏光顕微鏡観察、前記樹脂薄膜表面の走査型電子顕微鏡観察、および、前記樹脂薄膜断面の透過型電子顕微鏡観察によって、樹脂膜300の内部に、前記昇華性有機化合物が分子分散すなわち固溶化し、表面層が改質・着色されていることが確認された。また、得られた樹脂膜の表面および内部に、前記昇華性有機化合物の結晶は観察されなかった。

【0130】本実施例においては、密閉式容器内部100を減圧にしてから、加熱を行ったが、ヒーターを用いた真空中における加熱は「輻射熱」のみによって進行するため効率がよいとは言えない。特に、面積の大きい円形ガラス基板400および昇華源基板240を、それぞれ樹脂膜ガラス基板ヒーター740および昇華源基板ヒーター720に密着させ、伝熱をよくするためには熱伝導性シリコングリスなどを塗布する必要がある。そのようなものを用いずに、加熱工程の効率を高めるには、大気圧下で密閉式容器内部100、密閉式容器外壁110、および、真空弁190を所定の温度まで均一に加熱した後、密閉式容器内部100を所定の圧力まで減圧すればよい。大気圧下で加熱する際、空気中の酸素によって、樹脂や昇華性有機化合物が酸化劣化するおそれがある場合は、密閉式容器内部100の雰囲気を含め、窒素

ガスやアルゴンガスなどの不活性ガスで置換してから加熱すればよい。常圧において加熱すると気体量が減圧時に比べ多いため、気体分子の対流によって、密閉式容器内部全体を効率よく均一に加熱することができる。

【0131】なお、加熱を行ってから減圧する方法を採用する場合、所定の圧力まで減圧するのに要する時間が長いと、昇華性有機化合物からの昇華が始まってしまい、一部が真空排気系150へ逃げてしまう。この損失を最小限にするには、所定の圧力まで減圧するのに要する時間を極力短縮する必要がある。そのためには、真空弁190および真空配管系120の排気抵抗を小さくし、更に、真空排気系にターボ分子ポンプなどの高効率真空ポンプを用いればよい。

【0132】加熱後、減圧を行う手法を用いる際、予め昇華性有機化合物をシリカゲル、珪藻土、ゼオライトなどの多孔質粒子の孔内に含浸させて用いると、昇華した蒸気が孔内から密閉式容器内まで拡散するのに時間を要するため、減圧過程のロスを低減することが可能になる。

【0133】加熱後、減圧を行う手法を用いる際、昇華が始まると昇華源からは昇華する蒸気の量に応じた「昇華熱」が奪われる。これを補うため、昇華源に対して加熱を続け、温度制御を注意深く行う必要がある。一般に、昇華は沸騰ほど急速には進行しないため、真空中における加熱であっても、昇華熱の供給に遅滞が生ずるおそれは少ない。

【0134】密閉式容器内部を高速排気する場合、昇華性有機化合物が飛散しないよう工夫する必要がある。万一、昇華性有機化合物の粉末が樹脂成形物の表面に付着すると、昇華性有機化合物の粉末が直接樹脂膜中に浸透し、樹脂膜内への昇華性有機化合物の浸透・分散の均一性が損なわれるおそれがある。

【0135】昇華性有機化合物が飛散しないようにするためには、次に示すいずれかの構成からなる「昇華源」を用いればよい。

【0136】(A) 昇華性有機化合物が単独で昇華源基板の表面に塗工または成膜された膜、(B) 昇華性有機化合物とバインダー樹脂とが昇華源基板の表面に塗工または成膜された膜、(C) 昇華性有機化合物を含浸している多孔質粒子が昇華源基板の表面に塗工または成膜された膜、(D) 昇華性有機化合物を含浸している多孔質粒子とバインダー樹脂とが昇華源基板の表面に塗工または成膜された膜、(E) 多孔性の昇華源基板表面(例えば、アルマイト加工されたアルミニウム板)の孔に昇華性有機化合物が含浸されたもの。

【0137】成膜する際、バインダー樹脂を用いる場合は、原則として、昇華性有機化合物と親和性がないもしくは相溶性がなく、更に昇華性有機化合物を結晶または微粒子として分散させるものを選択して用いることが望ましい。これは、仮に、バインダー樹脂中に昇華性有機

化合物が固溶化してしまうと、厳密な意味での「昇華」が起こらなくなるからである。

【0138】成膜する際、塗工法を採用する場合は、塗工膜中に溶剤が残留しないよう、充分注意する必要がある。溶剤を用いた場合には、昇華性有機化合物が昇華しないような条件で塗膜中の残留溶媒を除去しなければならない。これは容易なことではないため、極力、溶媒を用いない塗工法、例えば、紫外線硬化型樹脂や電子線硬化型樹脂を用いた塗工法を採用することが望ましい。

【0139】昇華性有機化合物が溶融しやすい化合物である場合、無溶媒で昇華源基板上に溶融成膜する方法が推奨される。

【0140】昇華性有機化合物が溶融しやすい化合物であれば、上述した多孔質粒子や多孔質基板の孔中に、無溶媒で含浸させることができる。例えば、次に述べるような溶融法を用いることができる。すなわち、まず適量の高孔質粒子と昇華性有機化合物の微粉末を真空弁付き密閉式容器に仕込み、室温にて脱気を続け、多孔質粒子の孔内の空気を除去する。その後、密閉式容器を密閉し、加熱して、昇華性有機化合物を溶融させる。次いで、溶融状態のまま、密閉式容器内に不活性ガスを徐々に導入すると、溶融した昇華性有機化合物は多孔質粒子の孔内に浸透する。次いで、冷却した後、昇華性有機化合物によって凝集した昇華性有機化合物を含浸する多孔質粒子の塊を粉碎し、所望の粒径の昇華性有機化合物含浸多孔質粒子を得る。多孔質粒子の代わりに多孔質基板を用いて同様の工程を行い、最後に、多孔質基板表面に付着した昇華性有機化合物をかき落とせば、昇華性有機化合物含浸多孔質基板を得ることができる。

【0141】〔実施例6〕図6は、本実施例の樹脂表面層改質および/または着色装置の概略構成を示す断面図である。

【0142】昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する有機化合物20として、cis-1, 2-ジシアノー1, 2-ビス(2, 4, 5-トリメチル-3-チエニル)エテンをトレー24に入れ、真空扉CG1を通じて真空容器C1内へ導入した。真空扉CG1、真空弁CB1およびJC1を閉じることによって、真空容器C1の内部は閉じた空間Cとなる。

【0143】一方、樹脂成形物として、円形ガラス基板400(例えば、直径120mm、厚さ0.6mm)の1面にスピンコート法によってポリカーボネート樹脂のジクロロメタン溶液を塗工し、 $10^{-5}$ Paの高真空下、150℃で2時間脱気処理した樹脂膜300(膜厚1μm)をゲート弁JG1を通じ、移送レールJL1を利用して真空容器J1内へ導入した。ゲート弁JG1、真空弁JB1およびJC1を閉じることによって、真空容器J1の内部は閉じた空間Jとなる。

【0144】真空容器J1の内壁全面に取り付けられたヒーターJH1、ヒーター付きゲート弁JG1、およ



び、ヒーター付き真空弁JB1およびJC1による加熱を制御することによって、閉じた空間J内の温度を、閉じた空間C内の温度と同一の110℃に制御した。

【0145】また、真空容器C1の内壁全面に取り付けられたヒーターCH1、真空扉CG1用ヒーターCH2、および、ヒーター付き真空弁CB1およびJC1による加熱を制御することによって、閉じた空間C内の温度を、閉じた空間J内の温度と同一の110℃に制御した。実施例1に記載の通り、前記昇華性有機化合物は110℃において熱分解することなく昇華する。

【0146】真空容器C1に取り付けられたヒーター付き真空弁CB1を開いて真空排気系CV1へ接続することによって、閉じた空間C内の圧力を前記昇華性有機化合物の飽和昇華圧状態に置いた後、真空弁CB1を閉じた。なお、真空弁CB1を開いたままにすると、前記昇華性有機化合物の蒸気は真空排気系CV1へ逃げてしまう。そこで、真空装置各部からのリークによる減圧度の低下を補うため、時々真空弁CB1を開いて閉じた空間C内の圧力が前記昇華性有機化合物の飽和昇華圧となるよう制御した。

【0147】一方、真空容器J1に取り付けられたヒーター付き真空弁JB1を開いて真空排気系JV1へ接続することによって、閉じた空間J内の圧力を前記温度（110℃）における前記昇華性有機化合物の飽和昇華圧と同等以下とした後、真空弁JB1を閉じ、真空装置各部からのリークによる減圧度の低下を補うため、時々真空弁JB1を開いて閉じた空間J内の圧力が前記昇華性有機化合物の飽和昇華圧と同等以下となるよう制御した。

【0148】次いで、真空容器C1と真空容器J1を隔てているヒーター付き真空弁JC1を開き、閉じた空間Cと閉じた空間Jとを連結させて、閉じた空間Cと閉じた空間Jとを合わせた閉じた空間Mとし、更に、閉じた空間M内全体が前記有機化合物の飽和昇華圧状態になるよう温度および圧力を制御した。このようにして、連結前の閉じた空間C内に充満した前記昇華性有機化合物の蒸気が連結前の閉じた空間J内に拡散するようにした。この時、真空容器J1から真空排気系JV1への真空弁JB1を僅かに開き、真空容器J1内の圧力を真空容器C1内よりも低くなるように制御することによって、前記昇華性有機化合物の蒸気が真空容器C1から真空容器J1へ拡散する過程が促進される。ただし、真空弁JB1を開放したままにすると、前記昇華性有機化合物の蒸気は真空排気系JV1へ逃げてしまう。

【0149】以上のようにして、前記所定温度および圧力に制御することによって、真空容器C1内で発生させた前記昇華性有機化合物蒸気を、真空容器J1内に置いた前記樹脂成形物表面に均一に付着させ、付着した前記昇華性有機化合物を前記樹脂成形物表面から内部に浸透・分散させることができる。この工程を所定時間、例え

ば、10分継続させた後、真空容器C1と真空容器J1を隔てているヒーター付き真空弁JC1を閉じ、真空弁JB1を開いて真空容器J1内部に残留した前記昇華性有機化合物蒸気を排気し、真空容器J1の温度を室温近傍まで冷却した後、ゲート弁JG1をゆっくり僅かに開いて真空容器J1内部を大気圧に戻し、ゲート弁JG1を開放して前記樹脂成形物を取り出した。

【0150】得られた樹脂膜300の光吸収スペクトルの測定、光学顕微鏡観察（通常視野）、偏光顕微鏡観察、前記樹脂薄膜表面の走査型電子顕微鏡観察、および、前記樹脂薄膜断面の透過型電子顕微鏡観察によって、樹脂膜300の内部に、前記昇華性有機化合物が分子分散すなわち固溶化し、表面層が改質・着色されていることが確認された。また、得られた樹脂膜の表面および内部に、前記昇華性有機化合物の結晶は観察されなかった。

【0151】本実施例の装置（図6）を用い、上記の手順を遵守することによって、真空容器C1の温度を一定に保ったまま、真空容器C1内に仕込んだ昇華性有機化合物が完全に消費されるまで、連続的に樹脂成形物の表面を改質・着色することが可能になる。

【0152】〔実施例7〕図7は、本実施例の樹脂表面層改質および／または着色装置の概略構成を示す断面図である。

【0153】本実施例の樹脂表面層改質および／または着色装置は、実施例6の装置（図6）の真空容器J1に隣接して、ヒーター付きゲート弁JG1を介して真空容器J2を設けたものである。

【0154】樹脂成形物は真空扉JG2を通じ、真空容器J2内の移送レールJL2に乗せられる。ここで、真空扉JG2およびゲート弁JG1を閉じ、真空弁JB2を開き、真空排気系JV2によって真空容器J2内部の圧力を調整することによって、樹脂成形物処理用の真空容器J1内部の圧力を大気圧に戻すことなく、樹脂成形物を樹脂成形物処理用の真空容器J1内に導入することができる。

【0155】更に、以下に記述するような条件を満たすことによって、真空容器J2内部で昇華性有機化合物20が結晶化するようなトラブルなしに、真空容器J1および真空容器C1の温度を保ったまま、真空容器C1内に仕込んだ昇華性有機化合物が完全に消費されるまで、連続的に樹脂成形物の表面を改質・着色することが可能になる。

【0156】真空容器C1および真空容器J1の温度は昇華性有機化合物20の飽和昇華圧条件を満たすよう調節する。具体例は実施例6に記載の通りである。

【0157】ゲート弁JG1を開く場合、真空容器J2内は真空容器J1内部と同等の減圧度であり、真空弁JC1は閉じており、真空容器J1内部に昇華性有機化合物の蒸気が存在しないと言う条件を満たす必要がある。

この条件を満足しないと、真空容器J2内部で昇華性有機化合物20が結晶化する可能性がある。

【0158】真空容器J1内へ導入する樹脂成形物の温度は、導入前に所定の温度まで加熱されていることが好ましい。これは真空容器J1が減圧状態にあり、輻射熱による加熱しか有効でなく、昇温に実感を要するためである。具体的には、真空容器J2に導入する直前までに、大気圧下で所定温度まで加熱しておき、真空容器J2へ搬入後、速やかに減圧し、「真空保温状態」で真空容器J1内へ移送すればよい。

【0159】真空容器J1内で所定の時間処理された樹脂成形物を真空容器J2内へ移送してから大気中に取り出すには、次の手順で行うことが好ましい。まず、真空容器C1と真空容器J1を隔てているヒーター付き真空弁JC1を閉じ、真空弁JB1を開いて真空容器J1内部に残留した前記昇華性有機化合物蒸気を排気する。この間、真空容器J2内部の圧力をJ1内部と同等になるよう調整する。次いで、ゲート弁JG1を開き、樹脂成形物を真空容器J1内から真空容器J2内へ移送し、ゲート弁JG1を閉じる。樹脂成形物の温度が所定の温度まで下がった後、真空扉JG2を開いて樹脂成形物を大気中に取り出す。ここで注意する必要があるのは、減圧状態の真空容器J2内部において前記昇華性有機化合物が樹脂表面層から気化して脱離する現象である。飽和蒸気圧が高い有機化合物の場合、無視することはできない。これを防ぐには樹脂成形物の温度が室温よりも高い段階で真空容器J2内部へ空気または不活性気体を導入して大気圧下に戻し、樹脂成形物を急冷する手法が有効である。

【0160】〔実施例8〕図8は、本実施例の樹脂表面層改質および／または着色装置の概略構成を示す断面図である。

【0161】本実施例の樹脂表面層改質および／または着色装置は、実施例6の装置（図6）の真空容器J1に隣接して、ヒーター付きゲート弁JG1を介して真空容器J0を設け、更に、ヒーター付きゲート弁JG2を介して真空容器J2を設けたものである。本実施例の装置における真空容器J0は、樹脂成形物を装置に導入するに際し、実施例7（図7）における真空容器J2と同様の役割を果たすものであるが、樹脂成形物を真空容器J1へ移送するためだけに用いられる。本実施例の装置における真空容器J2は、樹脂成形物を装置外へ取り出すため、または、次の工程のための装置（図示せず）へ送るために用いられる。あるいは、真空装置J2内部に、例えばスパッタリング装置（図示せず）など、次工程のための装置を設けてもよい。

【0162】実施例7に記載した装置（図7）は樹脂成形物の表面改質・着色のみを行うのに適する。一方、本実施例の装置は、樹脂成形物の表面改質・着色に引き続き、別の加工工程へ樹脂成形物を連続的に移送するのに

適する。

【0163】樹脂成形物は真空扉JG0を通じ、真空容器J0内の移送レールJL0に乗せられる。ここで、真空扉JG0およびゲート弁JG1を閉じ、真空弁JB0を開き、真空排気系JV0によって真空容器J0内部の圧力を調整することによって、樹脂成形物処理用の真空容器J1内部の圧力を大気圧に戻すことなく、樹脂成形物を樹脂成形物処理用の真空容器J1内に導入することができる。

【0164】更に、以下に記述するような条件を満たすことによって、真空容器J0および／または真空容器J2内部で昇華性有機化合物20が結晶化するようなトラブルなしに、真空容器J1および真空容器C1の温度を保ったまま、真空容器C1内に仕込んだ昇華性有機化合物が完全に消費されるまで、連続的に樹脂成形物の表面を改質・着色することが可能になる。

【0165】真空容器C1および真空容器J1の温度は昇華性有機化合物20の飽和昇華圧条件を満たすよう調節する。具体例は実施例6に記載の通りである。

【0166】ゲート弁JG1を開く場合、真空容器J0内は真空容器J1内部と同等の減圧度であり、真空弁JC1は閉じており、真空容器J1内部に昇華性有機化合物の蒸気が存在しないと言う条件を満たす必要がある。この条件を満足しないと、真空容器J0内部で昇華性有機化合物20が結晶化する可能性がある。

【0167】真空容器J1内へ導入する樹脂成形物の温度は、導入前に所定の温度まで加熱されていることが好ましい。これは真空容器J1が減圧状態にあり、輻射熱による加熱しか有効でなく、昇温に実感を要するためである。具体的には、真空容器J0に導入する直前までに、大気圧下で所定温度まで加熱しておき、真空容器J0へ搬入後、速やかに減圧し、「真空保温状態」で真空容器J1内へ移送すればよい。

【0168】真空容器J1内で所定の時間処理された樹脂成形物を真空容器J2内へ移送してから大気中に取り出すには、次の手順で行うことが好ましい。まず、真空容器C1と真空容器J1を隔てているヒーター付き真空弁JC1を閉じ、真空弁JB1を開いて真空容器J1内部に残留した前記昇華性有機化合物蒸気を排気する。この間、真空容器J2内部の圧力をJ1内部と同等になるよう調整する。次いで、ゲート弁JG2を開き、樹脂成形物を真空容器J1内から真空容器J2内へ移送し、ゲート弁JG2を閉じる。樹脂成形物の温度が所定の温度まで下がった後、真空扉JG3を開いて樹脂成形物を大気中に取り出すか、または次の工程へ移送する。ここで注意する必要があるのは、減圧状態の真空容器J2内部において前記昇華性有機化合物が樹脂表面層から気化して脱離する現象である。飽和蒸気圧が高い有機化合物の場合、無視することはできない。これを防ぐには樹脂成形物の温度が室温よりも高い段階で真空容器J2内部へ

空気または不活性気体を導入して大気圧下に戻し、樹脂成形物を急冷する手法が有効である。

【0169】〔実施例9〕図9は、本実施例の樹脂表面層改質および/または着色装置の概略構成を示す断面図である。本実施例の装置は、実施例6の装置（図6）における移送レールの替わりにリール架台RH1およびRH2を樹脂成形物処理用の真空容器J1内部に取り付けたものであり、このリール架台に樹脂フィルムまたは繊維333を供給するための供給側リールR2および巻き取るための受側リールR1を取り付け、回転導入機（図示せず）などの機構によって受側リールを回転させることによって、樹脂フィルムまたは繊維333を連続的に処理するものである。

【0170】処理にあたっては、まず、昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する有機化合物20をトレー24に入れ、真空扉CG1を通じて真空容器C1内へ導入する。真空扉CG1、真空弁CB1およびJC1を閉じることによって、真空容器C1の内部は閉じた空間Cとなる。

【0171】一方、樹脂成形物として、供給側リールR2に巻き取られている樹脂フィルムまたは繊維333および受側リールR1をゲート弁JG1を通じて真空容器J1内へ導入し、それぞれリール架台RH2およびRH1へ取り付け、樹脂フィルムまたは繊維333が供給側リールR2から受側リールR1へ巻き取られるようにする。ゲート弁JG1、真空弁JB1およびJC1を閉じることによって、真空容器J1の内部は閉じた空間Jとなる。

【0172】真空容器J1の内壁全面に取り付けられたヒーターJH1、ヒーター付きゲート弁JG1、および、ヒーター付き真空弁JB1およびJC1による加熱を制御することによって、閉じた空間J内の温度を、閉じた空間C内の温度と同一の温度に制御する。この設定温度は昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する有機化合物20が熱分解せずに昇華する温度を下限とし、次の条件を満たす温度の内、最も高い温度を上限として、精密に温度制御する。

【0173】（a）昇華性有機化合物20の溶融開始温度を越えない温度、（b）前記樹脂のガラス転移温度、（c）前記樹脂の熱変形開始温度を越えない温度、（d）前記樹脂の溶融開始温度を越えない温度。

【0174】また、真空容器C1の内壁全面に取り付けられたヒーターCH1、真空扉CG1用ヒーターCH2、および、ヒーター付き真空弁CB1およびJC1による加熱を制御することによって、閉じた空間C内の温度を、閉じた空間J内の温度と同一の温度に制御する。

【0175】真空容器C1に取り付けられたヒーター付き真空弁CB1を開いて真空排気系CV1へ接続することによって、閉じた空間C内の圧力を昇華性有機化合物20の飽和昇華圧状態に置いた後、真空弁CB1を閉じ

る。なお、真空弁CB1を開いたままにすると、昇華性有機化合物20の蒸気は真空排気系CV1へ逃げてしまう。そこで、真空装置各部からのリークによる減圧度の低下を補うため、時々真空弁CB1を開いて閉じた空間C内の圧力が昇華性有機化合物20の飽和昇華圧となるよう制御する。

【0176】一方、真空容器J1に取り付けられたヒーター付き真空弁JB1を開いて真空排気系JV1へ接続することによって、閉じた空間J内の圧力を前記温度における昇華性有機化合物20の飽和昇華圧と同等以下とした後、真空弁JB1を閉じ、真空装置各部からのリークによる減圧度の低下を補うため、時々真空弁JB1を開いて閉じた空間J内の圧力が昇華性有機化合物20の飽和昇華圧と同等以下となるよう制御する。

【0177】次いで、真空容器C1と真空容器J1を隔てているヒーター付き真空弁JC1を開き、閉じた空間Cと閉じた空間Jとを連結させて、閉じた空間Cと閉じた空間Jとを合わせた閉じた空間Mとし、更に、閉じた空間M内全体が前記有機化合物の飽和昇華圧状態になるよう温度および圧力を制御する。このようにして、連結前の閉じた空間C内に充満した昇華性有機化合物20の蒸気が連結前の閉じた空間J内に拡散するようにする。この時、真空容器J1から真空排気系JV1への真空弁JB1を僅かに開き、真空容器J1内の圧力を真空容器C1内よりも低くなるように制御することによって、昇華性有機化合物20の蒸気が真空容器C1から真空容器J1へ拡散する過程が促進される。ただし、真空弁JB1を開放したままにすると、昇華性有機化合物20の蒸気は真空排気系JV1へ逃げてしまう。

【0178】昇華性有機化合物20の蒸気が充満した真空容器J1内において、受側リールを回転させて、樹脂フィルムまたは繊維333を一定速度、例えば10mm/分で供給側リールから受側リールへ移動させる。

【0179】以上のようにして、真空容器C1内で発生させた昇華性有機化合物20蒸気を、真空容器J1内に置いた樹脂フィルムまたは繊維333の表面に均一に付着させ、付着した昇華性有機化合物20を前記樹脂成形物表面から内部に浸透・分散させることができる。

【0180】供給側リールR2にて仕込んだ樹脂フィルムまたは繊維333の全部が受側リールR1に到達した後、真空容器C1と真空容器J1を隔てているヒーター付き真空弁JC1を閉じ、真空弁JB1を開いて真空容器J1内部に残留した昇華性有機化合物20蒸気を排気し、真空容器J1の温度を室温近傍まで冷却した後、ゲート弁JG1をゆっくり僅かに開いて真空容器J1内部を大気圧に戻し、ゲート弁JG1を開放してリールR1に巻き取られた樹脂フィルムまたは繊維333を取り出す。

【0181】本実施例の装置は繊維の表面層にフォトリソミック機能を付与させたり、プラスチックシート表面

層に紫外線吸収機能を付与させる目的で、特に好適に用いることができる。更に、プラスチックシート表面層に薬理活性機能や農薬としての機能を付与する目的にも用いることができる。

【0182】〔実施例10〕実施例9における樹脂フィルムまたは繊維333の代わりにプラスチック光ファイバーを用いる他は実施例9と同様にして、プラスチック光ファイバーの表面層を改質して、表面層の屈折率を変えたり、フォトクロミック機能や蛍光機能を付与したりすることができる。

【0183】〔実施例11〕実施例1において昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する有機化合物として用いた*cis*-1, 2-ジシアノ-1, 2-ビス(2, 4, 5-トリメチル-3-チエニル)エテンに替えて9, 10-ジフェニルアントラセンを用い、実施例1において樹脂成形物として用いたビスフェノールAポリカーボネートのペレットに替えて、ポリサルホン(アルドリッチケミカル株式会社製)のペレット(外径約2.5mm、長さ3mmの円柱状)を用い、実施例1における加熱温度110℃に替えて、処理温度を150℃とし、実施例1における処理時間24時間に替えて、処理時間を48時間とした他は実施例1と同様にして処理を行った。

【0184】このペレットを暗所に置き、紫外線ランプを照射すると、ペレット表面から鮮やかな青色蛍光が観察された。すなわち、ポリカーボネート樹脂の表面層に前記昇華性有機化合物が浸透・分散して、表面層が改質され、蛍光を呈する機能が付与されたことが判る。

【0185】〔実施例12〕図12は、本実施例の樹脂表面層改質および／または着色装置の概略構成を示す断面図である。この装置は粉末状樹脂の表面層改質および／または着色のために適するものである。

【0186】昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する有機化合物20として、*cis*-1, 2-ジシアノ-1, 2-ビス(2, 4, 5-トリメチル-3-チエニル)エテンをトレ-24に入れ、真空扉CG1を通じて真空容器C1内へ導入した。真空扉CG1、真空弁CB1およびJC1を閉じることによって、真空容器C1の内部は閉じた空間Cとなる。

【0187】一方、樹脂成形物として、熱硬化性アクリル変性樹脂微粉末「ラブコロール」(大日精化工業株式会社製)の無着色タイプ(平均粒子径20μm)を攪拌装置付真空扉JG4を通じ、真空容器J1内へ導入した。導入時、真空弁JC1およびJB1は完全に閉じておくものとする。なお、真空扉JG4、真空弁JB1およびJC1を閉じることによって、真空容器J1の内部は閉じた空間Jとなる。

【0188】大気圧下、すなわち、真空扉JG4を僅かに開いた状態で、真空容器J1の内壁全面に取り付けられたヒーターJH1、真空扉JG4用ヒーター、およ

び、ヒーター付き真空弁JB1およびJC1による加熱を制御することによって、閉じた空間J内の温度を、閉じた空間C内の温度と同一の110℃に制御した。更に、真空容器J1内の粉末状樹脂を、真空扉JG4に取り付けられたマグネットカップリング式攪拌モーターによって駆動される攪拌羽根を用い、粉末状樹脂全部が上記温度になるようかき混ぜた。粉末状樹脂の温度が上記温度に到達した後、真空扉JG4を完全に閉じた。

【0189】また、真空容器C1の内壁全面に取り付けられたヒーターCH1、真空扉CG1用ヒーターCH2、および、ヒーター付き真空弁CB1およびJC1による加熱を制御することによって、閉じた空間C内の温度を、閉じた空間J内の温度と同一の110℃に制御した。実施例1に記載の通り、前記昇華性有機化合物は110℃において熱分解することなく昇華する。

【0190】真空容器C1に取り付けられたヒーター付き真空弁CB1を開いて真空排気系CV1へ接続することによって、閉じた空間C内の圧力を前記昇華性有機化合物の飽和昇華圧状態に置いた後、真空弁CB1を閉じた。なお、真空弁CB1を開いたままにすると、前記昇華性有機化合物の蒸気は真空排気系CV1へ逃げてしまう。そこで、真空装置各部からのリークによる減圧度の低下を補うため、時々真空弁CB1を開いて閉じた空間C内の圧力が前記昇華性有機化合物の飽和昇華圧となるよう制御した。

【0191】一方、真空容器J1内の粉末状樹脂を、真空扉JG4に取り付けられたマグネットカップリング式攪拌モーターによって駆動される攪拌羽根を用いてかき混ぜながら、真空容器J1に取り付けられたヒーター付き真空弁JB1を少しずつ開いて真空排気系JV1へ接続することによって、閉じた空間J内の圧力を前記温度(110℃)における前記昇華性有機化合物の飽和昇華圧と同等以下とした。この際、急激に真空弁JB1を開くと、粉末状樹脂が激しく舞い上がるので注意が必要である。次いで、真空弁JB1を閉じ、真空装置各部からのリークによる減圧度の低下を補うため、時々真空弁JB1を開いて、閉じた空間J内の圧力が前記昇華性有機化合物の飽和昇華圧と同等以下となるよう制御した。

【0192】次に、真空容器C1と真空容器J1を隔てているヒーター付き真空弁JC1を開き、閉じた空間Cと閉じた空間Jとを連結させて、閉じた空間Cと閉じた空間Jとを合わせた閉じた空間Mとし、更に、閉じた空間M内全体が前記有機化合物の飽和昇華圧状態になるよう温度および圧力を制御した。また、真空容器J1内の粉末状樹脂を、真空扉JG4に取り付けられたマグネットカップリング式攪拌モーターによって駆動される攪拌羽根を用いてかき混ぜ続けた。このようにして、連結前の閉じた空間C内に充満した前記昇華性有機化合物の蒸気が連結前の閉じた空間J内に拡散するようにした。この時、真空容器J1から真空排気系JV1への真空弁J

B1を僅かに開き、真空容器J1内の圧力を真空容器C1内よりも低くなるように制御することによって、前記昇華性有機化合物の蒸気が真空容器C1から真空容器J1へ拡散する過程が促進される。ただし、真空弁JB1を開放したままにすると、前記昇華性有機化合物の蒸気は真空排気系JV1へ逃げてしまう。

【0193】以上のようにして、前記所定温度および圧力に制御することによって、真空容器C1内で発生させた前記昇華性有機化合物蒸気を、真空容器J1内でかき混ぜられた粉末状樹脂の表面に均一に付着させ、付着した前記昇華性有機化合物を前記樹脂成形物表面から内部に浸透・分散させることができる。この工程を所定時間、例えば、12時間継続させた後、真空容器C1と真空容器J1を隔てているヒーター付き真空弁JC1を閉じ、真空弁JB1を開いて真空容器J1内部に残留した前記昇華性有機化合物蒸気を排気し、真空容器J1の温度を室温近傍まで冷却した後、真空扉JG4をゆっくり僅かに開いて真空容器J1内部を大気圧に戻し、真空扉JG4を完全に開放して前記樹脂成形物を取り出した。

【0194】得られた粉末状樹脂の光学顕微鏡および走査型顕微鏡観察によって、粉末状樹脂の表面全体が均一に、前記フォトリソミック化合物によって着色されていることが確認された。また、粉末状樹脂中に、フォトリソミック化合物の微結晶の存在は確認されなかった。

【0195】得られた粉末状樹脂は、紫外線をカットした可視光線および／または赤外線の照射で黄色に、紫外線の照射によって赤色に変化する。すなわち、粉末状樹脂の表面層が改質されたことによって、粉末状フォトリソミック樹脂として機能することが確認された。

【0196】〔実施例13〕樹脂成形物として、実施例6における円形ガラス基板400の1面に形成されたポリカーボネート樹脂薄膜に替えて、ポリ(メタクリル酸メチル)製のプラスチックレンズを用い、前記プラスチックレンズの縁を保持する架台を利用した他は実施例6と同様にして、プラスチックレンズの表面層を前記フォトリソミック色素を用いて改質し、フォトリソミック機能を付与した。

【0197】前記プラスチックレンズの代わりにガラスレンズの表面が樹脂コーティングされたものを用いても、同様にして、表面層を前記フォトリソミック色素を用いて改質し、フォトリソミック機能を付与することができる。

【0198】また、昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する有機化合物として、前記フォトリソミック色素の代わりに、通常の昇華性色素を用いることによって、プラスチックレンズまたは樹脂コートレンズの表面層を改質して、任意の色に着色することもできる。

【0199】〔実施例14〕容量50mlのスクリーバイアル内に、樹脂成形物としてビスフェノールAポリ

カーボネート(アルドリッチケミカル株式会社製)のペレット(外径約2.5mm、長さ2.5mmの円柱状)5~6個と、昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する有機化合物20としてフェロセンカルボキシアルデヒド(アルドリッチケミカル株式会社製;融点117℃)の結晶とを設置し、スクリーバイアルの蓋を封印し、前記スクリーバイアルを120℃に温度設定した恒温槽へ入れ、大気圧下で加熱した。スクリーバイアル内部の温度上昇にともないフェロセンカルボキシアルデヒドの昇華が始まり、内部は飽和蒸気圧状態に到達する。加熱を4時間続けた後、室温まで4時間を要して冷却した。

【0200】得られたポリカーボネートペレットの表面層は、フェロセン誘導体特有の鮮やかな橙色に着色されていた。

【0201】得られたポリカーボネートペレットの断面を走査型電子顕微鏡に取り付けたX線マイクロアナライザーで観察・分析したところ、ペレットの表面から約10マイクロメートルの深さにわたって鉄元素が分布していることが確認された。すなわち、前記樹脂ペレットの内部に、前記昇華性有機化合物が分子分散すなわち固溶化し、表面層が改質・着色されていることが確認された。

【0202】〔実施例15〕樹脂成形物として市販のポリプロピレン製衣装用ハンガー10個およびガラス製蒸発皿に入れた樟脳(mp178℃;和光純薬製)20gを真空乾燥機(ヤマト科学製DP41型)の中へ入れ、真空扉を密閉し、吸気口の真空弁を完全に閉じ、排気口の真空弁を僅かに開いた状態で加熱を始め、内部壁面温度が100℃に到達したとき排気口の真空弁を完全に閉じて密閉状態とし、内部温度が100℃ないし105℃になるよう温度を制御しながら加熱を続けた。真空乾燥機の観察窓からガラス製蒸発皿中の樟脳を観察し、完全に昇華した後、2時間、内部温度を前記温度範囲に保った。次いで、加熱を止め、12時間放冷した後、吸気口を開いて内部圧力を大気圧にしてから真空扉を開いてハンガーを取り出した。真空乾燥機の内部およびハンガーの表面に、樟脳の結晶は析出していなかった。ハンガーの重量を1個ずつ計量したところ、平均2g、重量が増加していた。ハンガーの表面層に樟脳が浸透・分散して重量が増加したものと判断される。このようにして表面層が改質されたポリプロピレン製衣装用ハンガーは、樟脳が有する防虫機能を長期間発揮する。

【0203】〔比較例3〕ポリプロピレン中に樟脳を混練して射出成型を試みたが、樟脳の昇華による減量が著しく、組成が一定した成形物を得ることは困難であった。また、作業環境中に大量の樟脳蒸気が発生するため、作業環境および大気保全のためには新たに局所排気装置および排気処理装置が必要となることが判った。

【0204】次に、樟脳のトルエン溶液にポリプロピレ

ン製衣装用ハンガーを浸して表面層に樟脳を含浸させる方法を試みた。ある程度の量の樟脳が含まれることは確認されたが、溶剤として用いたトルエンもポリプロピレン中に浸透してしまうため、そのままでは日用品用として使用することができない。そこで、真空乾燥機中、60℃で長時間加熱減圧乾燥を行い、トルエンを完全に除去したところ、ハンガー中の樟脳重量は、実施例15の場合の1/50程度であった。実施例15の方法に比べて著しく効率が悪いことが判った。

#### 【0205】

【発明の効果】以上、詳細に説明したように、本発明の樹脂成形物表面層の改質方法およびそのための装置および表面層が改質された樹脂成形物、および樹脂成形物表面層の着色方法およびそのための装置および表面層が着色された樹脂成形物、および表面層の改質により機能性を付与された樹脂成形物によれば、昇華性有機化合物と樹脂からなり、これらの組成が均一な、改質された表面層を樹脂成形物の表面に作製すること、昇華性有機化合物を含有し、かつ、揮発性の不純物を含まない、改質された表面層を樹脂成形物の表面に作製すること、昇華性有機化合物と樹脂からなり、これらの組成が均一な、改質された表面層を樹脂成形物の表面に効率よく作製すること、樹脂成形物の表面平滑性を損なわずに、昇華性有機化合物を含有した、改質された表面層を樹脂成形物の表面に作製すること、樹脂成形物の表面に微細加工が施されている場合、この表面構造を損なわずに、昇華性有機化合物を含有した、改質された表面層を樹脂成形物の表面に作製すること、広範な種類の昇華性有機化合物を含有した、改質された表面層を樹脂成形物の表面に作製すること、複雑な機械的制御なしに、膜厚および／または組成が均一な昇華性有機化合物を含有した、改質された表面層を樹脂成形物の表面に作製すること、表面層の面積の大小に関わらず、均一な膜厚および／または組成を有する昇華性有機化合物を含有した、改質された表面層を樹脂成形物の表面に作製すること、および、上記の特徴を有する改質された表面層を持つ樹脂成形物を提供することが可能になる。

【0206】さらに、昇華性色素と樹脂からなり、これらの組成が均一な、着色された表面層を樹脂成形物の表面に作製すること、昇華性色素を含有し、かつ、揮発性の不純物を含まない、着色された表面層を樹脂成形物の表面に作製すること、昇華性色素と樹脂からなり、これらの組成が均一な、着色された表面層を樹脂成形物の表面に効率よく作製すること、樹脂成形物の表面平滑性を損なわずに、昇華性色素を含有した、着色された表面層を樹脂成形物の表面に作製すること、樹脂成形物の表面に微細加工が施されている場合、この表面構造を損なわずに、昇華性色素を含有した、着色された表面層を樹脂成形物の表面に作製すること、広範な種類の昇華性色素を含有した、着色された表面層を樹脂成形物の表面に作

製すること、複雑な機械的制御なしに、膜厚および／または組成が均一な昇華性色素を含有した、着色された表面層を樹脂成形物の表面に作製すること、表面層の面積の大小に関わらず、均一な膜厚および／または組成を有する昇華性色素を含有した、着色された表面層を樹脂成形物の表面に作製すること、上記の特徴を有する着色された表面層を持つ樹脂成形物、および、表面層が改質されたことによって、表面層が機能性を付与された樹脂成形物を提供することができる。

【0207】また、樹脂全体に機能性材料を混練して機能性を付与する場合よりもはるかに少ない機能性材料の使用量で、樹脂成形物の表面層に機能性を付与することができる。

#### 【図面の簡単な説明】

【図1】 実施例1の樹脂表面層改質・着色方法の1段階における樹脂表面層改質・着色装置の概略構成を示す断面図である。

【図2】 実施例1の樹脂表面層改質・着色方法の1段階における樹脂表面層改質・着色装置の概略構成を示す断面図である。

【図3】 実施例1の樹脂表面層改質・着色方法の1段階における樹脂表面層改質・着色装置の概略構成を示す断面図である。

【図4】 実施例2の樹脂表面層改質・着色方法における樹脂表面層改質・着色装置の概略構成を示す断面図である。

【図5】 実施例5の樹脂表面層改質・着色方法における樹脂表面層改質・着色装置の概略構成を示す断面図である。

【図6】 実施例6の樹脂表面層改質・着色方法における樹脂表面層改質・着色装置の概略構成を示す断面図である。

【図7】 実施例7の樹脂表面層改質・着色方法における樹脂表面層改質・着色装置の概略構成を示す断面図である。

【図8】 実施例8の樹脂表面層改質・着色方法における樹脂表面層改質・着色装置の概略構成を示す断面図である。

【図9】 実施例9の樹脂表面層改質・着色方法における樹脂表面層改質・着色装置の概略構成を示す断面図である。

【図10】 実施例1で得られた樹脂ペレットの断面を光学顕微鏡で拡大して観察した状況を示す図である。図中のスケールの1目盛は10μmである。

【図11】 実施例2で作製したフォトリソミック樹脂薄膜へ紫外線を照射したときのスペクトル変化を示す図である。

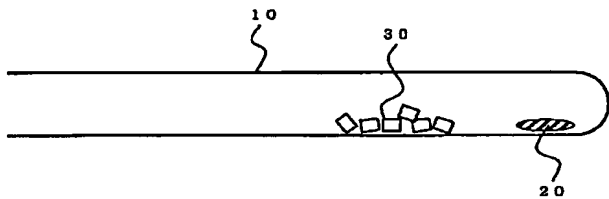
【図12】 実施例12の樹脂表面層改質・着色方法における樹脂表面層改質・着色装置の概略構成を示す断面図である。

## 【符号の説明】

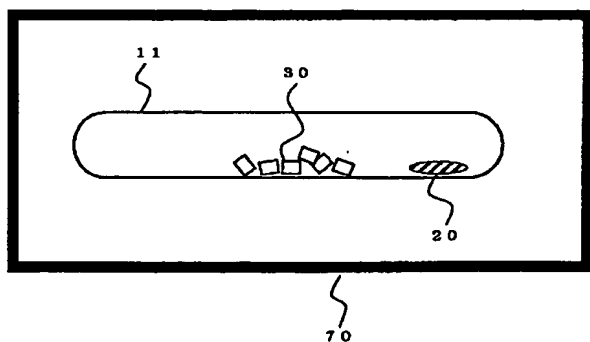
10 一端を封じたガラス管、11 両端を封じたガラス管、20 昇華性を有しかつ被覆される樹脂成形物の樹脂と親和性を有する有機化合物、24 トレー、30 樹脂ペレット、33 樹脂薄膜、40 ガラス基板、50 真空排気装置、60 ガラス管封管用パーナー、70 恒温槽、100 密閉式容器内部、110 密閉式容器外壁、120 真空配管系、150 真空排気系、190 真空弁、200 成膜された昇華性有機化合物、240 昇華源基板、300 樹脂膜、303 粉末状樹脂、333 樹脂フィルムまたは繊維、400 円形ガラス基板、710 ヒーター、720 昇華源基板ヒーター、740 樹脂膜ガラス基板ヒーター、790 真空弁ヒーター、C1 真空容器（昇華源用）、CB1 ヒーター付き真空弁、CG1 ヒーター付き真空

扉、CH1 C1用ヒーター、CH2 CG1用ヒーター、CV1 C1用真空排気系、J0 真空容器（ロードロック室）、J1 真空容器（樹脂成形物処理用）、J2 真空容器（樹脂成形物後処理用）、JB1およびJC1 ヒーター付き真空弁、JB0およびJB2 真空弁、JG0 J0用真空扉、JG1およびJG2 ヒーター付きゲート弁、JG3 ゲート弁、JG4 攪拌装置付真空扉、JH1 J1用ヒーター、JH4 JG4用ヒーター、JL0およびJL1およびJL2 移送レール、JM1 マグネットカップリング式攪拌モーター、JV0 J0用真空排気系、JV1 J1用真空排気系、JV2 J2用真空排気系、R1 受側リール、R2 供給側リール、RH1およびRH2 リール架台、TB1 攪拌羽根。

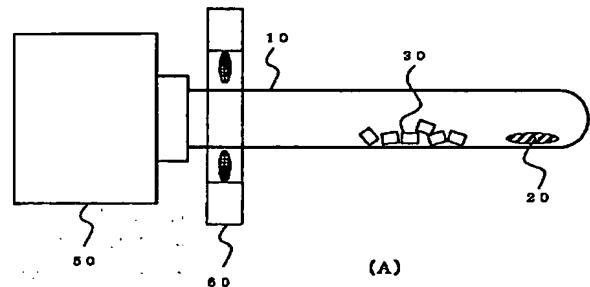
【図1】



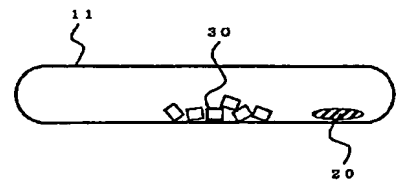
【図3】



【図2】

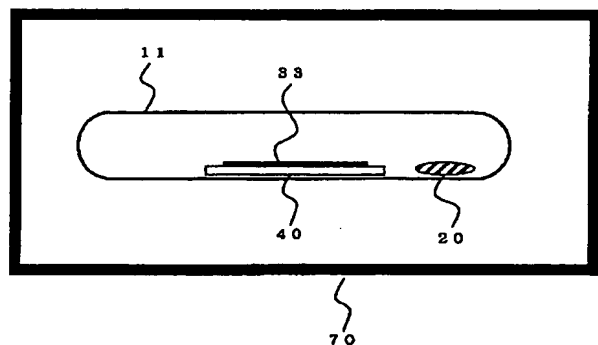


(A)

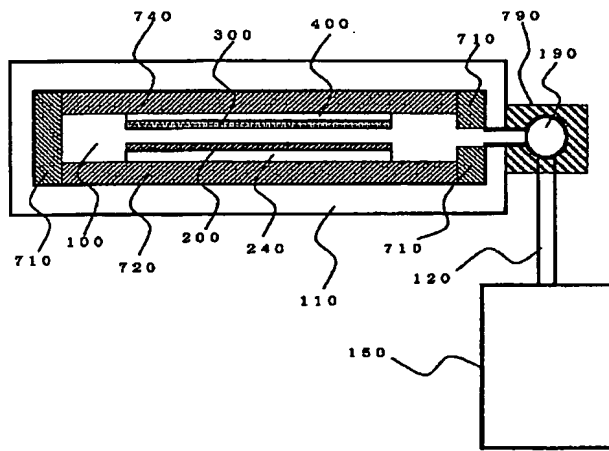


(B)

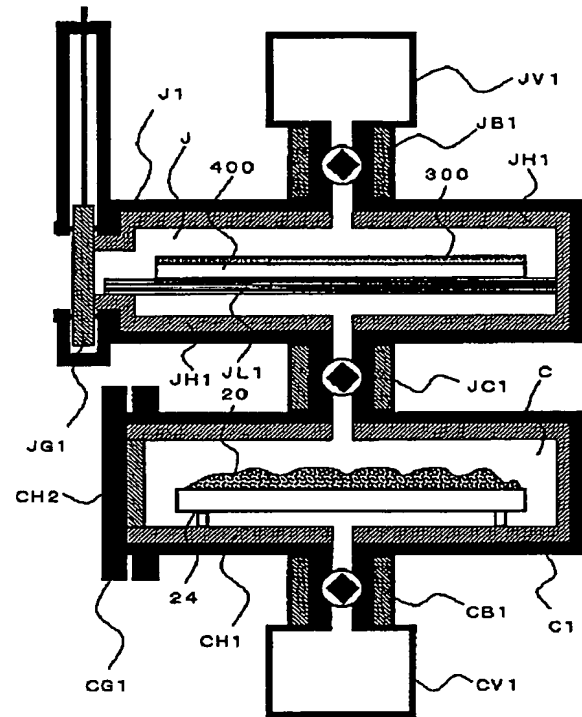
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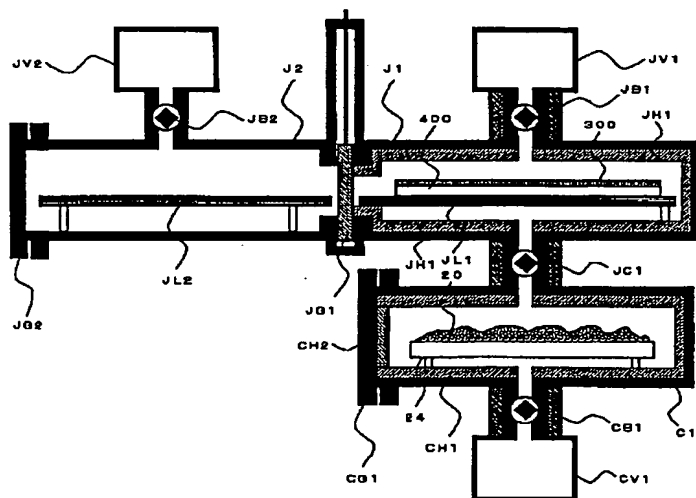
【図5】



【図6】

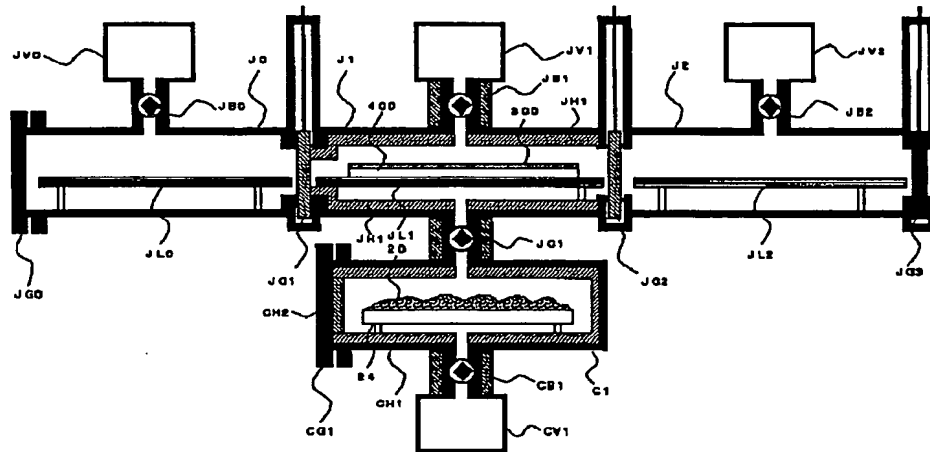


【図7】

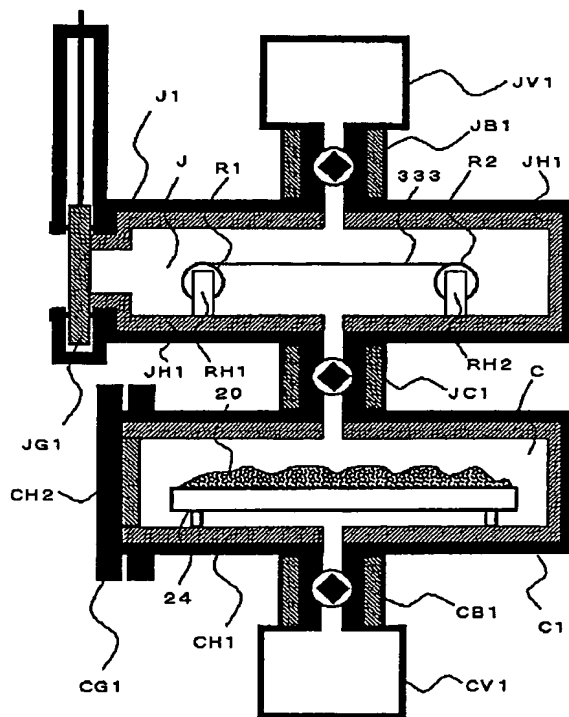




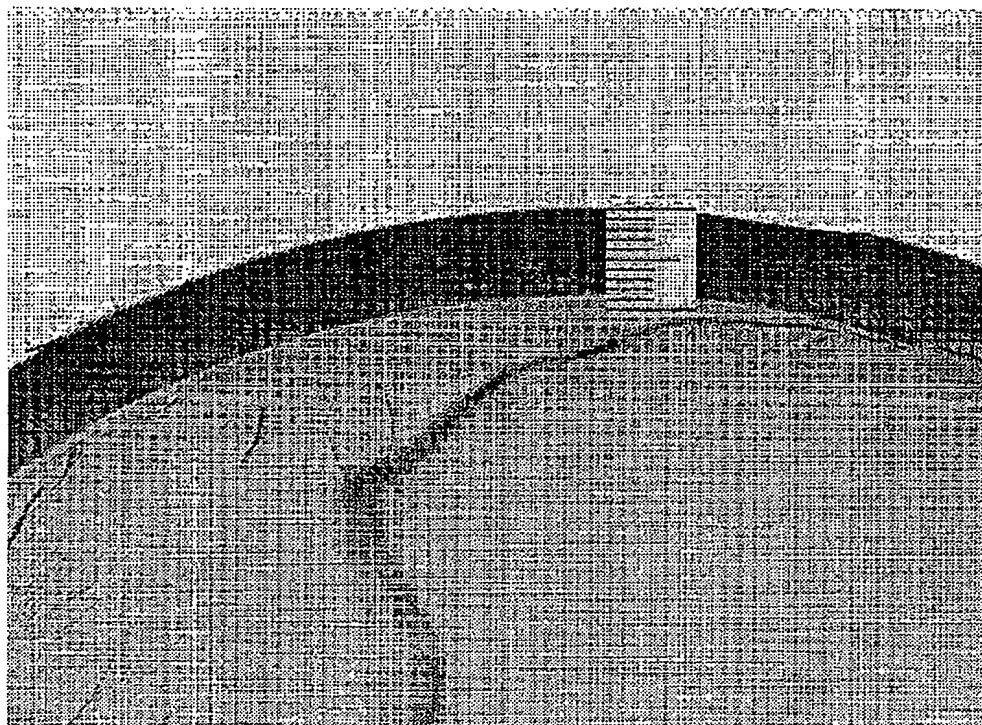
【図8】



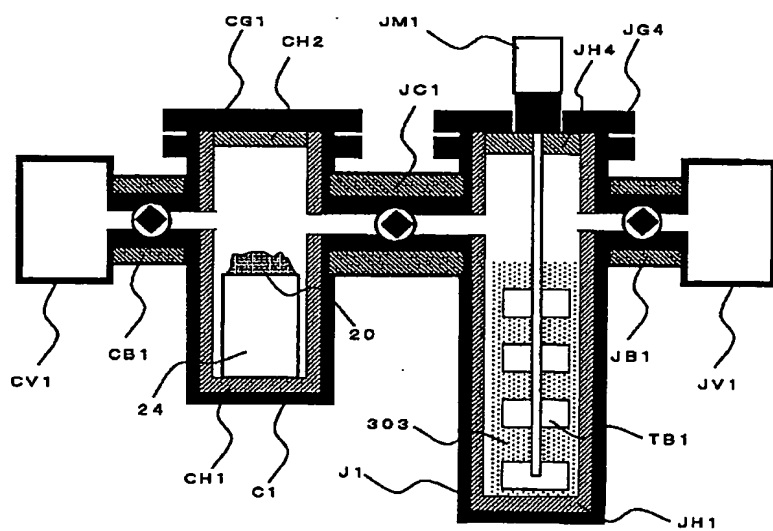
【図9】



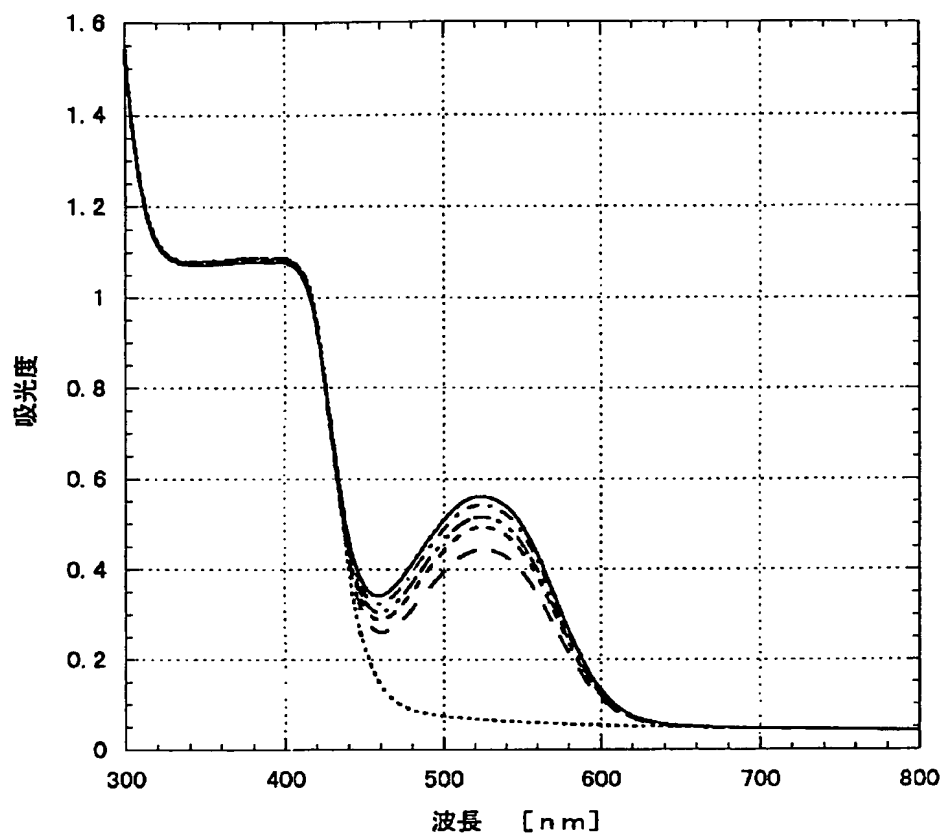
【図10】



【図12】



【図11】



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4C076 AA71 EE03 EE12  
4F006 AA04 AA12 AA13 AA15 AA16  
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AB64 AB65 AB68 BA01 BA17  
CA05 CA06 DA05 EA02 EA05  
4F201 AD08 AD11 AD16 AG01 AH74  
AH75 AH77 AR02 AR06 BA07  
BC01 BC02 BC12 BC13 BC15  
BR37 BT02  
4L031 CA06 CA09 DA00 DA09

(54) 【発明の名称】 樹脂成形物表面層の改質方法およびそのための装置および表面層が改質された樹脂成形物、および樹脂成形物表面層の着色方法およびそのための装置および表面層が着色された樹脂成形物、および表面層の改質により機能性を付与された樹脂成形物

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